Syntheses in the Fluoranthene Series.

- by -

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C O N T E N T S

INTRODUCTION

Fluoranthene is a polycyclic aromatic hydrocarbon. Although it was first discovered in 1877, its constitution was not proved until 1929. As a result, much of the early work is rather obscure. Most of the work on this hydrocarbon has been carried out in the last 20 years.

Discovery.

While Bödecker (2) was working with a mixture of high-boiling hydrocarbons which he obtained from the smelting of mercurial ores of Idria, he isolated what he thought to be a pure hydrocarbon which he called Idryl.

Later Goldschmiedt (19,20,21) examined this fraction more carefully and was able to isolate from the crude Idryl of Bödecker the following hydrocarbons:- anthracene, phenanthrene, pyrene, chrysene and a new hydrocarbon to which he gave the name Idryl. This hydrocarbon had the same percentage composition as the crude Idryl (namely $C_{15}H_{10}$) but had different properties.

At the same time, Fittig and Gebhard (13,14), working independently from Goldschmiedt, isolated from a coal tar fraction a hydrocarbon which proved to be identical with Goldschmiedt's Idryl. Their analysis

supported the formula $C_{15}H_{10}$. In view of the relationship of phenanthrene to diphenyl, and of the new hydrocarbon to fluorene, Fittig and Gebhard named it fluoranthene. This name has subsequently been retained in preference to Idryl.

Sources.

In recent times, fluoranthene has been obtained by means other than those adopted by Goldschmiedt, and Fittig and Gebhard.

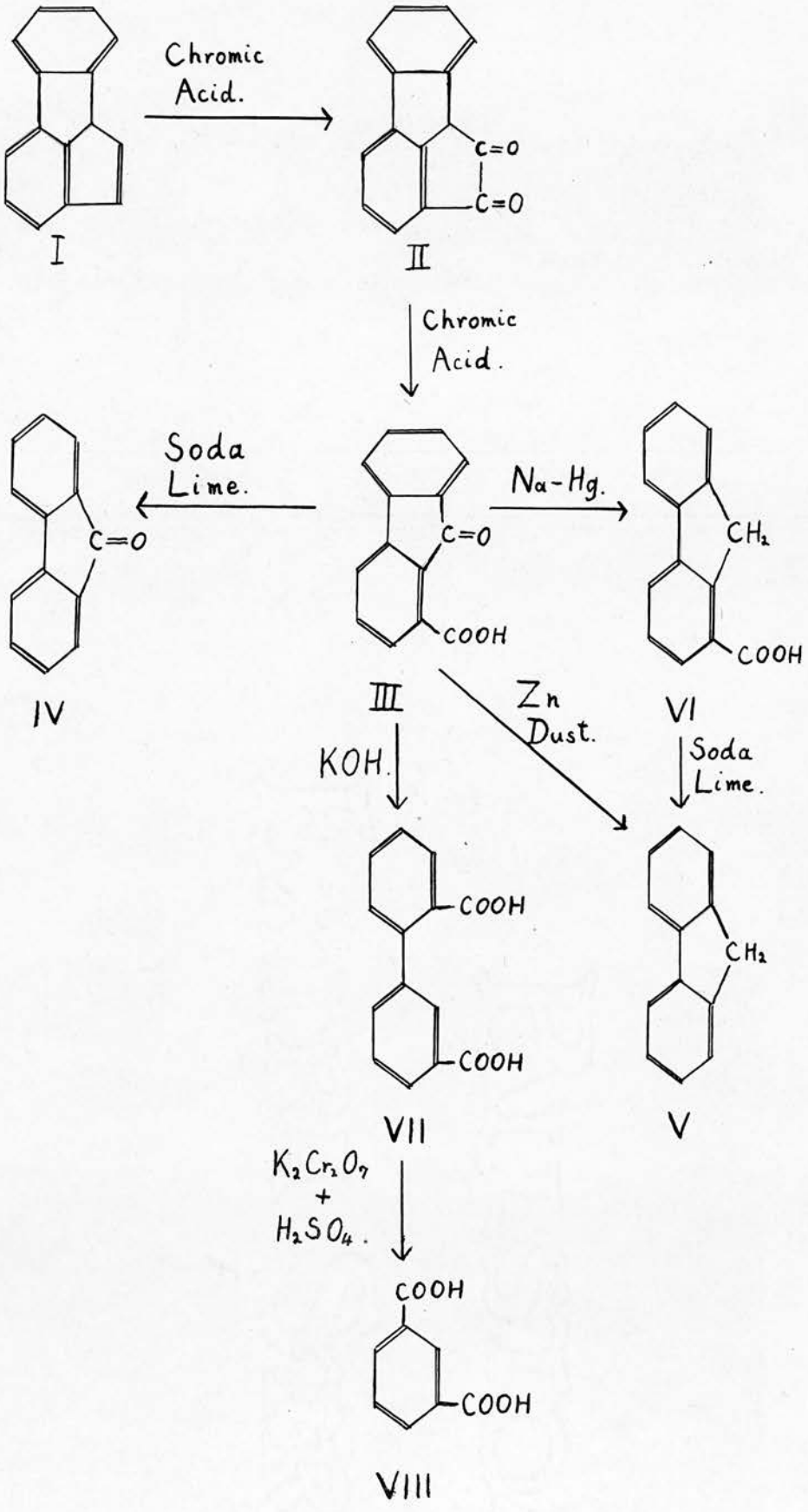
Kruber (22) obtained fluoranthene on a large scale from coal tar by stirring a dilute benzene solution of the neutral tar-oil fraction (b.p. 370° - 390°C) with sodium at 160°C. He thereby obtained a tetrasodio derivative of fluoranthene which yielded tetrahydrofluoranthene on treatment with water. Various means can be used to dehydrogenate this compound to fluoranthene. Ber., 1931, 64, 82. ?

Fluoranthene has also been obtained from the destructive hydrogenation of coal tar (10,11,12).

The synthetic methods of preparing fluoranthene will be described later.

Structure.

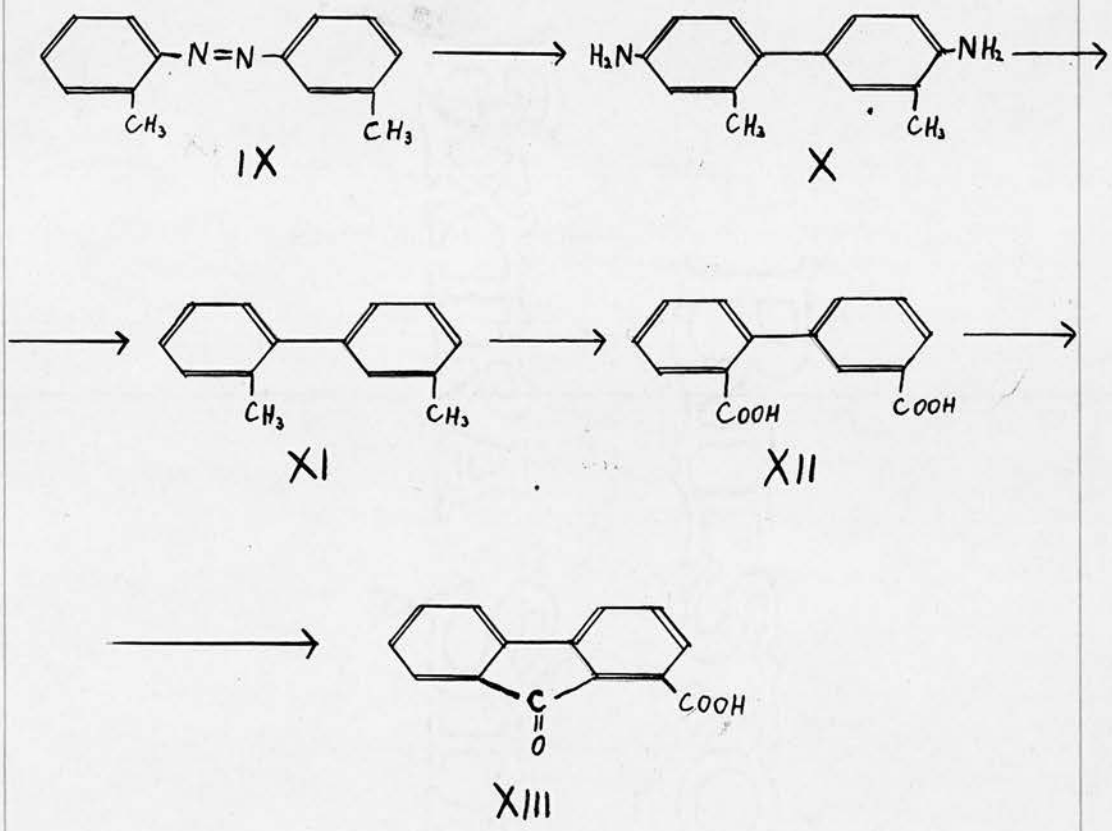
Fittig and Gebhard (13,14) advanced the structural formula I for fluoranthene after a study of the following reactions. On oxidation with chromic acid, fluoranthene gave fluoranthene quinone II and a fluorenone-carboxylic


Chromic Acid.
C=O
C=O
I
II
Chromic Acid.
Soda Lime.
Na-Hg.
C=O
COOH
CH₂
COOH
IV
III
VI
Zn Dust.
KOH.
Soda Lime.
COOH
COOH
CH₂
VII
V
K₂Cr₂O₇ + H₂SO₄.
COOH
COOH
VIII

acid III. When this acid was heated with soda lime, fluorenone IV was obtained. When the acid was distilled with zinc dust, fluorene V was isolated in good yield. Fluorenone-carboxylic acid on reduction with sodium amalgum gave a fluorene-carboxylic acid VI which could be easily converted into fluorene V by distilling with soda lime. Fusion of fluorenone-carboxylic acid with potassium hydroxide gave isodiphenic acid VII which on oxidation with potassium dichromate in sulphuric acid yielded isophthalic acid VIII. From these results, Fittig and Gebhard concluded that fluoranthene must be represented by the structural formula I; fluoranthene quinone by II; and the fluorenone-carboxylic acid by III. The work of Fittig and Liepmann (15,16) supported these conclusion.

Further support was given by Mayer and Freitag (24) when they prepared fluorenone-1-carboxylic acid by two different methods and showed it to be identical with the fluorenone-carboxylic acid obtained by Fittig and Gebhard. The first method involved the following steps. 2-3'-dimethylazobenzene IX was converted into 4:4'-diamino-2:3'-dimethyldiphenyl X by stannous chloride in hydrochloric acid. The amino groups were removed to give 2:3'-dimethyldiphenyl XI. This hydrocarbon was oxidised by potassium permanganate to diphenyl-2:3'-

dicarboxylic acid XII which was converted by concentrated sulphuric acid into fluorenone-1-carboxylic acid XIII.

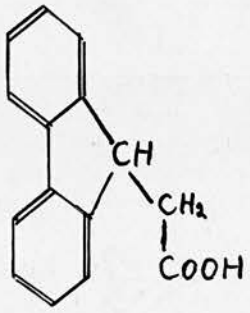


The second synthesis involved an Ullmann reaction between o-iodotoluene and m-iodotoluene. An oil was obtained which, after repeated distillation, was oxidised with potassium permanganate. From the resulting products, an acid, identical with the diphenyl-2:3'-dicarboxylic acid obtained before, was isolated by extraction with water.

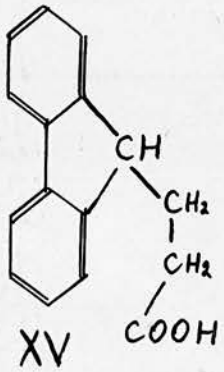
Mayer (23) failed to synthesise fluoranthene by ring closure of 9-fluorenylacetic acid XIV with (a)

zinc chloride at 160° C., (b) phosphorus pentachloride, (c) action of aluminium chloride in nitrobenzene on the acid chloride, (d) heating the acid chloride at 200°C. He obtained only indefinite products which on zinc dust distillation gave fluorene.

He also acted on the acid chloride of 9-fluorenyl-propionic acid XV with aluminium chloride in light petroleum but was unable to detect any cyclisation.

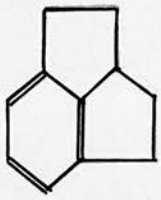


XIV

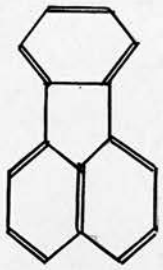


XV

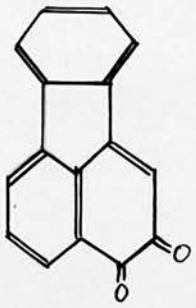
In 1929, von Braun and Anton (3) applied the Baeyer theory of stability of fused ring systems to fluoranthene. According to this theory, two 5-membered rings could be fused together to give a stable compound only if the fusion occurred in the 'cis' position and neither 5-membered ring deviated from the plane model. These conditions could not be satisfied if the two rings were fused adjacently to a benzene nucleus to form a tricyclic compound XVI. Stable tricyclic systems can be formed by fusion onto a benzene nucleus of adjacent 5- and 6-, 6- and 7-, or two 6-membered rings.



XVI



XVII



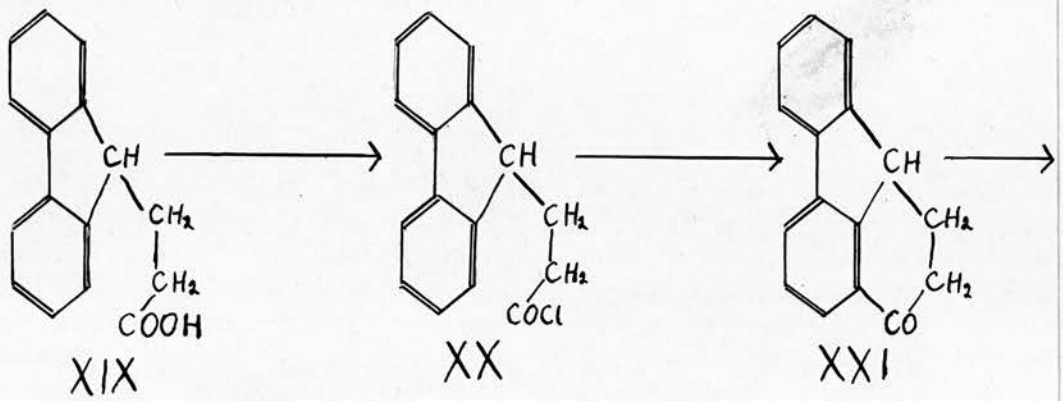
XVIII

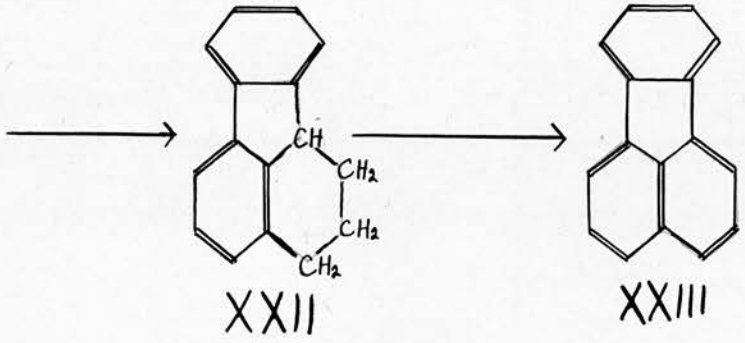
Thus the indene type of structure I suggested by Fittig and Gebhard would not yield a stable compound. However, if fluoranthene was regarded as a naphthalene derivative XVII, it would be expected to be quite stable. Fluoranthene quinone would then be given the structure XVIII. Von Braun and Anton pointed out that the analysis figures for fluoranthene and fluoranthene quinone agree with those required by the two proposed structures.

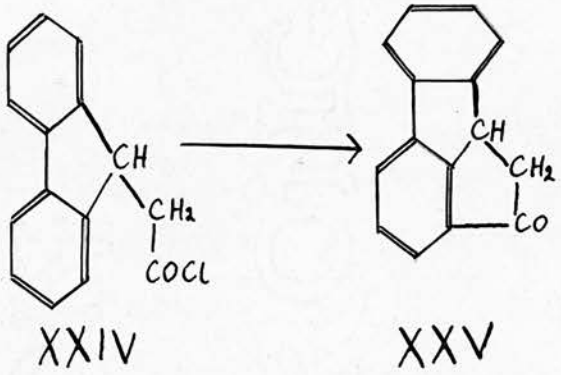
Consequently von Braun and Anton decided to repeat the work of Mayer (23) and showed that formula XVII was the correct one by synthesising fluoranthene. β-9-fluorenylpropionic acid XIX was converted into β-9-fluorenylpropionyl chloride XX by thionyl chloride. Cyclisation was effected by aluminium chloride in light petroleum to give 4-keto-1:2:3:4-tetrahydrofluoranthene XXI which, on reduction with zinc amalgum and hydrochloric acid, gave 1:2:3:4-tetrahydrofluoranthene XXII. Lead oxide dehydrogenated this compound to give fluoranthene XXIII.

An attempt to synthesise the corresponding keto indene compound XXV failed as 9-fluorenylacetyl chloride

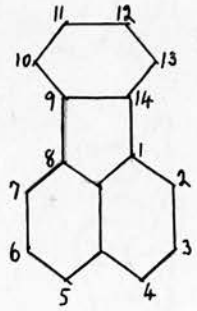
XXIV could not be cyclised.







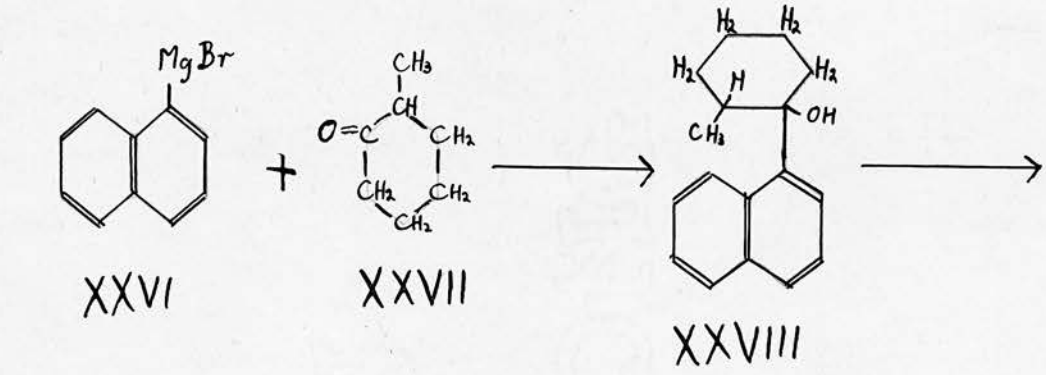
The numbering of the fluoranthene nucleus throughout this thesis conforms to that in general use, viz.



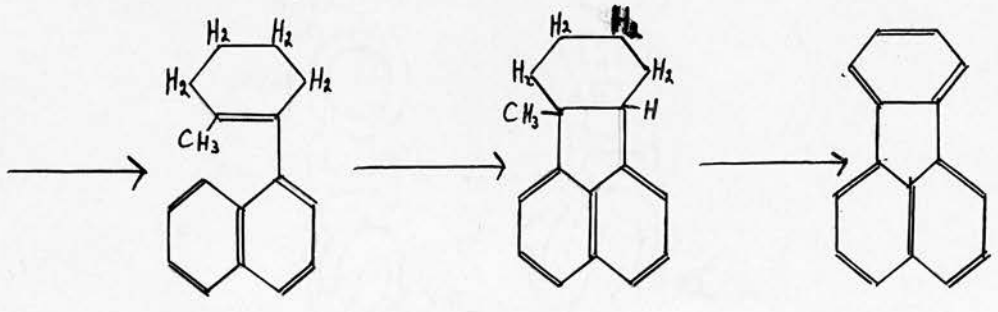
Syntheses.

Following the work of von Braun and Anton, fluoranthene has been synthesised by other methods.

Cook and Lawrence (7) condensed 1-naphthyl magnesium bromide XXVI with 2-methylcyclohexanone XXVII to give 1-(1'-naphthyl)-1-hydroxy-2-methylcyclohexanone XXVIII. This carbinol was dehydrated with potassium hydrogen sulphate to give 1-(1'-naphthyl)-2-methyl-Δ^{1}-cyclohexene XXIX. When cyclisation was carried out in carbon disulphide at 0°C, 9:10:11:12:13:14-hexahydro-9-methylfluoranthene XXX was obtained as an oil, which was dehydrogenated by heating at 310°C - 320°C with selenium to give fluoranthene XXXI in poor yield.

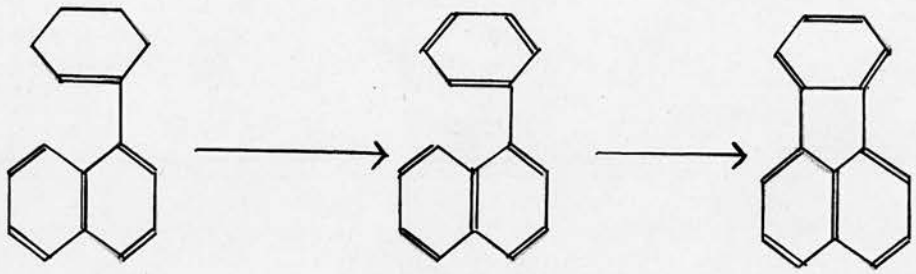


XXVI XXVII XXVIII



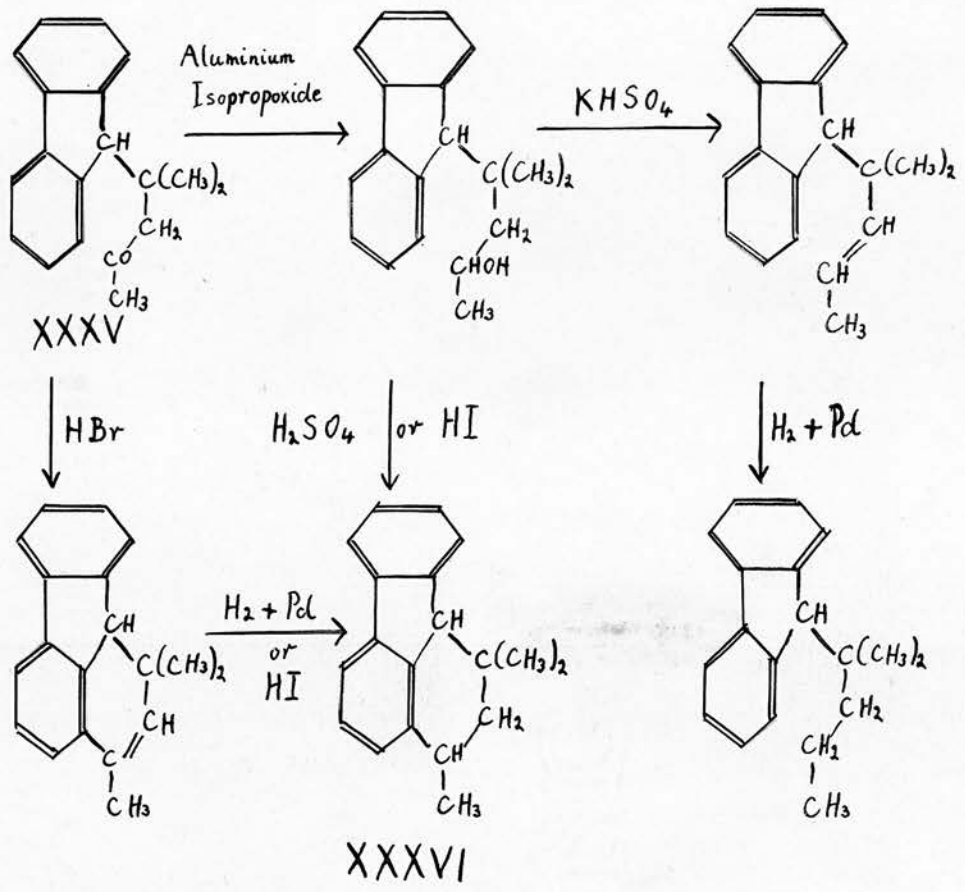
XXIX XXX XXXI

Orchin and Reggel (25) prepared 1-(Δ'-cyclohexene)-naphthalene XXXII in a similar manner by condensing 1-naphthyl magnesium bromide with cyclohexanone. They dehydrogenated this compound to give 1-phenylnaphthalene XXXIII. Fluoranthene XXXIV was obtained by cyclodehydrogenation over palladium charcoal or in better yield by a mixture of chromic anhydride and alumina.



XXXII XXXIII XXXIV

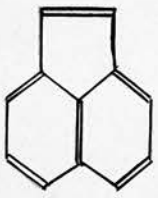
France, Maitland and Tucker (17) condensed fluorene with acetone in presence of potassium hydroxide to give methyl β-9-fluorenyl-β-methyl-n-propyl ketone XXXV. This compound was later used by France, Tucker and Forrest (18) to synthesise 1:2:3:4-tetrahydro-2:2:4-trimethyl-fluoranthene XXXVI according to the following stages.



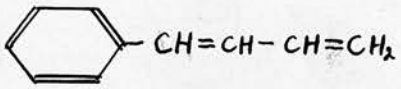
XXXV

XXXVI

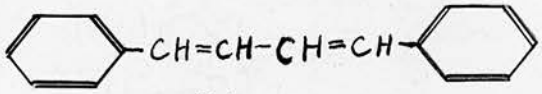
Some substituted fluoranthenes have recently been synthesised by Bergmann (1). Acenaphthylene XXXVII undergoes a Diels-Alder addition with 1-phenyl-$\Delta^{1:3}$-butadiene XXXVIII and 1:4-diphenyl-$\Delta^{1:3}$-butadiene IXL to give the hydrocarbons XL and XLI respectively when the reactants are heated to 160°C - 200°C. 2:3:4:5:2':3':4':5'-octahydrodiphenyl XLII also acts as a diene and the reaction is accompanied by partial dehydrogenation to give the hydrocarbon XLIII.



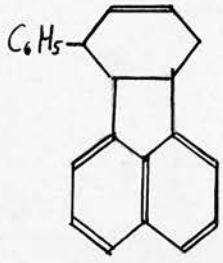
XXXVII



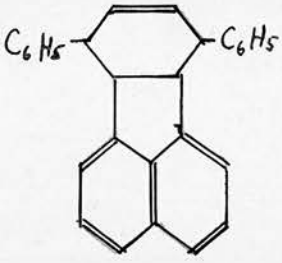
XXXVIII



IXL

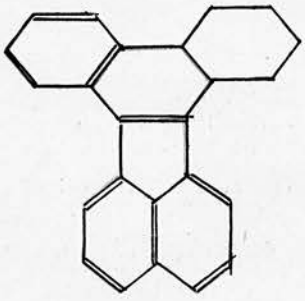


XL



XLI

XLII



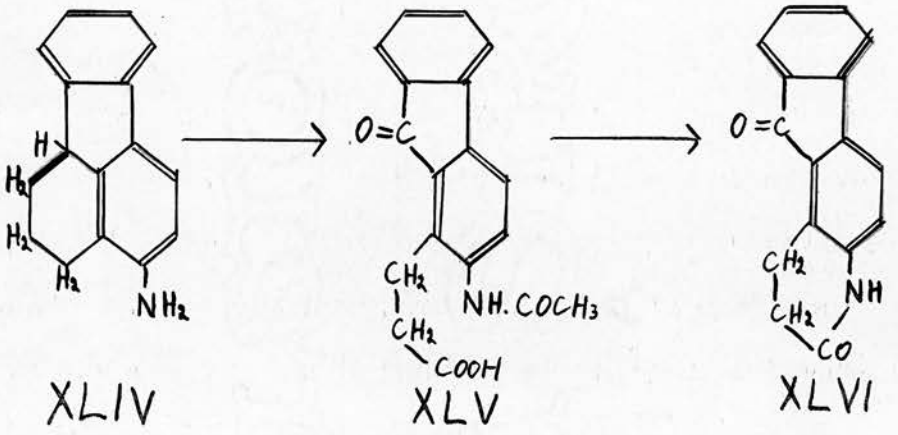
XLIII

Substitution.

Goldschmiedt (19) described the preparation of a bromo compound, quinone and a picrate. Fittig and Gebhard (13, 14) formed a trinitro derivative along with the oxidation products described earlier. Except for this work, no other derivative was prepared nor any attempt made to find out the positions of the substituents, until von Braun and Manz (5) systematically examined the

chemistry of fluoranthene in 1931. They found that monobromination, -nitration and -sulphonation proceeded mainly in the 4-position accompanied by a little in the 11-position. Von Braun, Manz and Kratz (6) found that the Friedel-Crafts reaction gave mainly the 11-isomer along with small amounts of the 4-.

Monobromofluoranthene, purified via the picrate, gave a cyano derivative with copper cyanide. The monosulphonic acid could be converted into this cyano compound by heating with sodium and potassium cyanide. The cyano derivative can be hydrolysed to the carboxylic acid which can be converted into the phenol via the amide. The phenol with ammonia in alcohol gave the amine. This amine can also be formed by reduction of the nitro derivative. Reduction of the amine with sodium amalgum gave a tetrahydro compound XLIV, the acetyl derivative of which on oxidation gave the keto acid XLV. On deacetylation, the acid changed spontaneously into the lactam XLVI showing that the amino substituent must be in position 4 since lactam formation would not have been possible with the group in any other position.



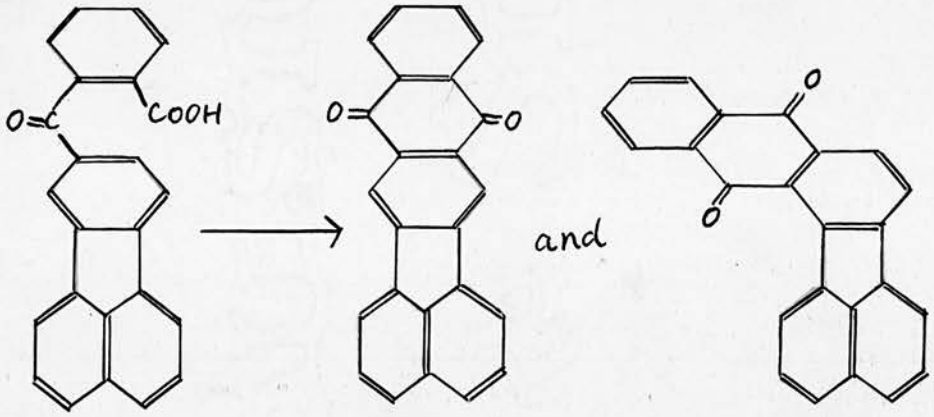
XLIV XLV XLVI

A Friedel-Crafts reaction of oxalyl chloride on fluoranthene gave as the main product a monocarboxylic acid which on oxidation with chromic acid gave a mixture of two fluorenone-dicarboxylic acids. The possibility of two oxidation products is only possible if substitution had occurred in the 10- or 11-positions. This acid was converted into the amine via the hydrazide, azide and urethane. This amine was isomeric to the 4-amino-fluoranthene prepared before.

In the Friedel-Crafts reaction, benzoyl chloride and phthalic anhydride gave a benzoylfluoranthene and an o-carboxybenzoylfluoranthene XLVII respectively. The oximes of these compounds underwent Beckmann re-arrangements and hydrolyses to give an amine identical with that obtained from the above fluoranthenecarboxylic acid, and consequently are probably 10- or 11-.

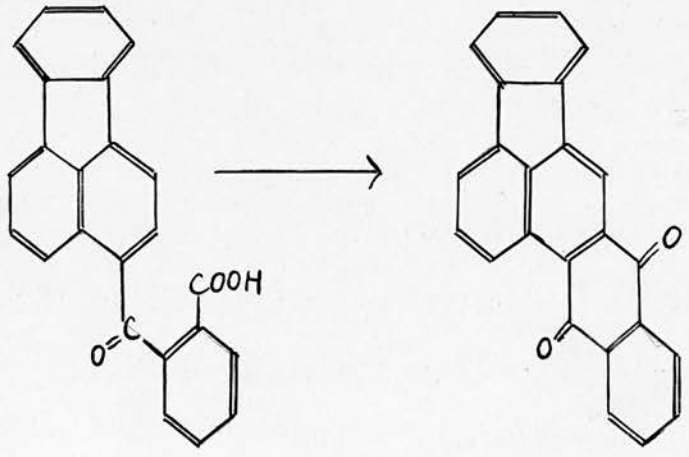
They found that o-carboxybenzoylfluoranthene XLVII could be cyclised by heating the acid chloride in tri-chlorobenzene to give two quinones XLVIII and IL. If

substitution had occurred in the 10-position, only one quinone IL would have been possible. Therefore substitution must have occurred in the 11-position.



XLVII XLVIII IL

The Friedel-Crafts reaction is accompanied by some of the 4-isomer. The 4-o-carboxybenzoylfluoranthene L can be cyclised by sulphuric acid to the quinone LI.



L LI

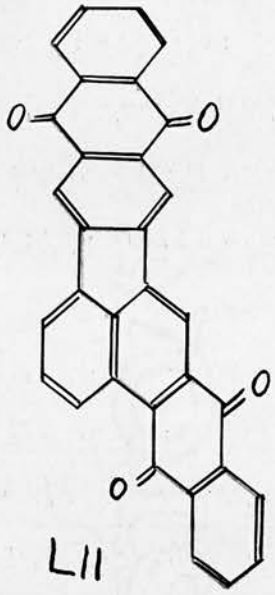
The orientation of disubstituted derivatives of fluoranthene has been tackled but the evidence is not conclusive. By analogy to monosubstituted compounds, it seemed probable that substitution occurred in the 4:11- or 4:12-positions.

Von Braun, Manz and Kratz (5,6) described the preparation of a disulphonic acid of fluoranthene. Later work (8,9) showed that this acid on fusion with potassium hydroxide gave the dihydroxy derivative which could be easily oxidised to a compound which appeared to be a quinone. A quinonoid structure would only be possible if substitution had occurred in the 4:11-positions. A quinone grouping would be impossible with a 4:12-derivative.

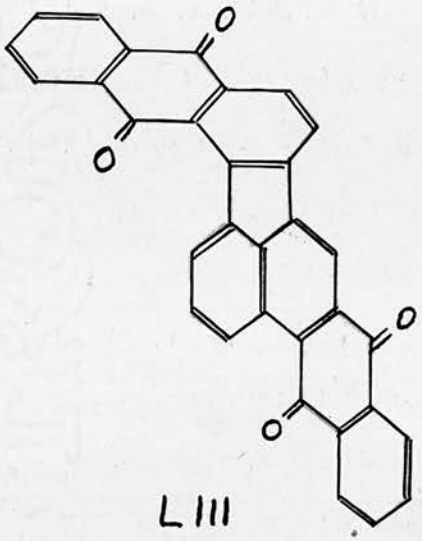
Dibromofluoranthene has been prepared by Goldschmiedt (20), von Braun, Manz and Kratz (5,6) and Tobler, Holbro, Sutter and Kern (26). By analogy with the disulphonic acid, it was concluded that this was the 4:11- derivative.

Von Braun, Manz and Kratz (6) found that the Friedel-Crafts reaction gave some disubstitution besides monosubstitution. Thus they prepared compounds which were probably fluoranthene-4:11-dicarboxylic acid, 4:11-dibenzoylfluoranthene and 4:11-di-o-carboxybenzoylfluoranthene. From the latter they were able to prepare the

two quinones LII and LIII.



LII



LIII

Attempts to synthesise simple disubstituted fluoranthenes of known constitution have proved unsuccessful. For example, Tobler, Holbro, Sutter and Kern (26), starting with 2:7-dibromofluorene and following an analogous procedure to the synthesis of fluoranthene (3), failed to obtain 4:11-dibromofluoranthene.

Fluoranthene also undergoes trisubstitution, but the positions of substitution are not known with any certainty.

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OBJECT OF RESEARCH

It was felt that the orientation of fluoranthene derivatives required clarification and confirmation by syntheses. The syntheses already reported are tedious, give poor yields and cannot be applied generally to produce substituted fluoranthenes. A synthesis capable of general application would be a big advance in fluoranthene chemistry.

The object of this research was to investigate routes to the synthesis of fluoranthene, keeping in view the possibility of extension of such a synthesis. The present work has been carried out with fluorene as the starting material since many substituted fluorenes are known and have been fully orientated.

EXPERIMENTAL

Introduction

All melting points quoted are uncorrected and were determined on the apparatus described in "Qualitative Organic Analysis" (p.7, fig. 4) by N. Campbell.

The yields were calculated as the percentage of the maximum theoretically possible.

Analyses were carried out by Drs. Weiler and Strauss, Oxford by micro methods.

(A) DARZENS' SYNTHESIS

I. Preparation of 9-fluorenylallylacetic acid.

1st Stage:- Preparation of fluorenone.

The oxidation was carried out in the manner described by Huntress, Hershberg and Cliff (J.A.C.S., 1931, 53, 2720).

Fluorene (50 g.) on oxidation with sodium dichromate (150 g.) gave fluorenone which was recrystallised from benzene.

m.p. 83° - 84°C. lit. m.p. 84°C.
Yield 40 g. 74%.

2:4-dinitrophenylhydrazone-orange needles m.p. 299° - 301°C. The only m.p. quoted in the literature for this compound is by Cliff M.I.T., Ph.D. Thesis - m.p. 284°C (uncorr.).

Analysis (of 2:4-dinitrophenylhydrazone). fd. N=15·3%
$C_{19}H_{12}O_4N_4$ requires N=15·55%

2nd Stage:- Preparation of 9-fluorenol.

The reduction was carried out by a modification by Fairfull (Ph.D. Thesis. Edin. Univ. 1948) of the method of Werner and Grob. (Ber., 1904, 37, 2896.) Better

yields were obtained on increasing the quantity of alcohol and decreasing the concentrated ammonia.

25 g. fluorenone.
125 c.c. alcohol.
125 c.c. concentrated ammonia.

This solution was refluxed in a three necked flask while dry ammonia gas was passed in. Zinc dust (100 - 200 g.) was added in small portions. The solution turned dark brown and later colourless. When a white precipitate began to appear, the solution was filtered hot from the zinc. On cooling, the filtrate deposited 9-fluorenol, which was filtered, dried and recrystallised from benzene in white plates.

m.p. 152° - 3°C. lit. m.p. 153°C.
Yield 20 g. 79%.

3rd Stage:- Preparation of 9-bromofluorene.

The reaction was carried out according to the method of Staudinger (Ber., 1906, 39, 3060,) who, however, did not give full details.

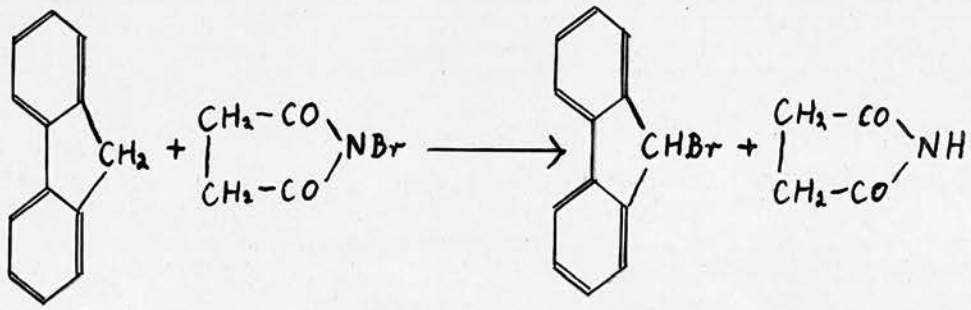
A suspension of 25 g. 9-fluorenol in 150 c.c. glacial acetic acid was saturated with dry hydrogen bromide gas. The solution was then heated at its boiling-point for 3 minutes, still with the hydrogen bromide gas passing. The solution was cooled and the 9-bromo-

fluorene precipitated by the addition of water. The solid was recrystallised from light petroleum (b.p. 80° - 100°) in colourless needles.

m.p. 103° - 104°C. lit. m.p. 104°C.

Yield. 22 g. 66%.

9-Bromofluorene was also prepared direct from fluorene by the method of Wittig and Felletschine (Ann., 1944, 555, 133). N-Bromosuccinimide was used as brominating agent.



The reaction did not proceed smoothly unless the N-bromosuccinimide was very pure. Ziegler et al. (Ann., 1942, 551, 109) found that it was essential to employ a 99% preparation. When the N-bromosuccinimide was purified according to the method of Ziegler, the reaction proceeded without difficulty.

5 g. fluorene

5·4 g. N-bromosuccinimide

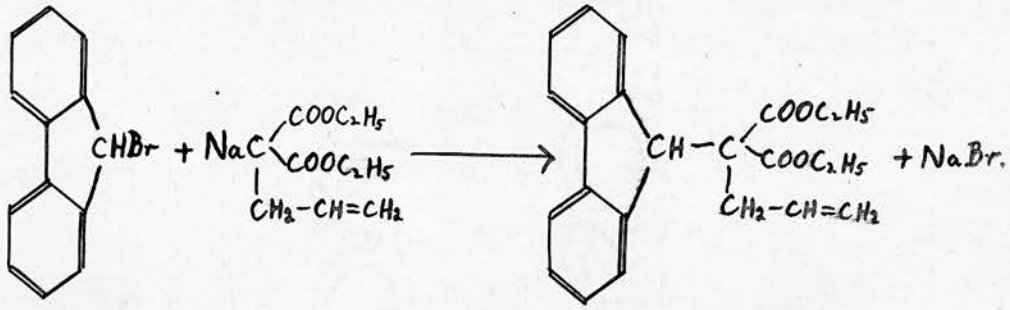
20 c.c. carbon tetrachloride.

This mixture was refluxed for 3 hours. The solution was cooled, the succinimide formed was filtered off, and the filtrate evaporated to dryness. The residue was recrystallised from light petroleum (b.p. 60°-80°) in long needles.

m.p. 101° - 104°C. lit. m.p. 104°C.

Yield 2·6 g. 35%.

4th Stage:- Preparation of diethyl 9-fluorenylallylmalonate.



16·34 g. 9-bromofluorene.

13·2 g. diethyl allylmalonate.

1·55 g. sodium.

45 c.c. alcohol (absolute).

The alcohol was placed in a 3 necked flask fitted with a stirrer, condenser, and a dropping funnel. The sodium was slowly added, the flask being cooled if the

reaction became too violent. The malonic ester derivative was gradually added to the warm sodium ethoxide solution, and, almost immediately, the clear liquid turned into a white semi-solid mass. The 9-bromofluorene was then slowly added. The mixture was refluxed until the solution was no longer alkaline to moist litmus paper (about 6 hours). Sodium bromide crystallised out during the reaction. Most of the alcohol was then distilled off from a water bath, and the semi-solid residue shaken up with warm water. The sodium bromide dissolved and the oil was taken up in ether. The ether layer was separated, washed 4 times with warm water, and dried with anhydrous sodium sulphate. On removal of the ether, a thick viscous brown oil was obtained which did not solidify in a freezing mixture and which could not be distilled under reduced pressure without decomposition.

Yield 15 g. (crude) 82%.

All malonic ester condensations conducted were effected in a similar manner to the above experiment. The reaction usually required 2 hours refluxing. The purification of the product varied with its nature. If diethyl malonate was used in the reaction, this was

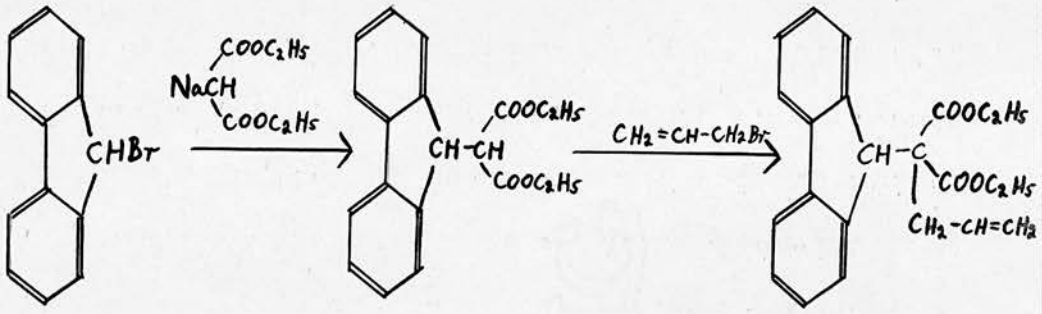
distilled under reduced pressure before use.

The diethyl allylmalonate used in the above experiment was prepared from malonic ester and allyl bromide and the oil was distilled under reduced pressure.

b.p. 124°-128° C/30 mm.

Yield 75%.

Diethyl 9-fluorenylallylmalonate was also prepared by condensing 9-bromofluorene first with malonic ester and then with allyl bromide.



Both condensations were effected in the normal manner. Diethyl 9-fluorenylmalonate was obtained as an oil which solidified on cooling in ice. Three crystallisations from aqueous alcohol gave colourless needles.

Yield 67%.

m.p. 68° - 69° C.

Diethyl 9-fluorenylmalonate has been prepared but

not isolated by Bachmann and Sheehan (J.A.C.S., 1940, 62, 2687).

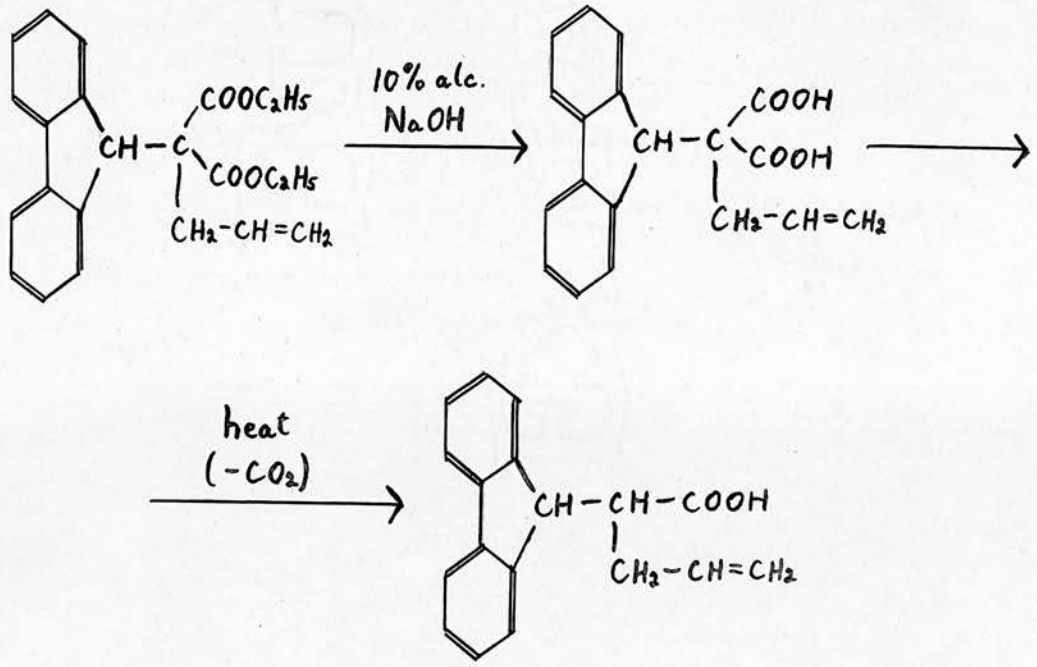
Analysis fd. C = 73·95% H = 6·21%.

$C_{20}H_{20}O_4$ requires C = 74·06% H = 6·22%.

Diethyl 9-fluorenylallylmalonate was obtained as an oil which did not solidify in a freezing mixture and which could not be distilled under reduced pressure.

Both these oils on subsequent hydrolysis and decarboxylation gave the same product, namely:- 9-fluorenylallylacetic acid (m.p.'s were the same and mixed m.p. gave no depression).

5th Stage:- Preparation of 9-fluorenylallylacetic acid.



Diethyl 9-fluorenylallylmalonate (15 g.) was hydrolysed by refluxing for 2 hours with 50 c.c. 10% alcoholic sodium hydroxide. A white salt-like compound was obtained which was filtered off. This was dissolved in water and, on acidification with dilute hydrochloric acid, gave a little effervescence of carbon dioxide and a brown oil which solidified on cooling.

m.p. 170°C. with evolution of carbon dioxide.

This solid was heated to 170° - 180°C. until all evolution of carbon dioxide had ceased. The oil on cooling solidified and was recrystallised twice from light petroleum (b.p. 100° - 120°). Colourless needles.

m.p. 128° - 129°C.

Yield 4·25 g. 39%

Analysis. fd. C = 81·32% H = 6·32%

$C_{18}H_{16}O_2$ requires C = 81·80% H = 6·10%

Properties. A cold alcoholic solution of the acid decolourised aqueous potassium permanganate showing the presence of a double bond.

The acid was easily soluble in cold sodium carbonate solution.

II. Attempted ring closure of 9-fluorenylallylacetic acid.

The ring closure of 9-fluorenylallylacetic acid was tried using varying conditions but without success. When sulphuric acid was used as the cyclisating agent, the starting compound was obtained in many cases. If more drastic conditions were used sulphonation occurred as shown by the solubility of the product in water.

The following conditions were tried.

Strength of H_2SO_4 (by weight)	Temperature	Time	Result
65%	100° C	6 hrs.	Unchanged.
65%	140° -150° C	6 "	Sulphonation with charring.
60%	140° -150° C	5 "	Sulphonation with charring.
50%	130° -140° C	4 "	Sulphonation.
80%	cold	24 "	Unchanged.
80%	cold	14 days	Unchanged.
80%	50° -55° C	6 hrs.	Sulphonation.

Where the unchanged compound was obtained, it was identified by m.p. and mixed m.p. No fluorescence was observed.

Where sulphonation occurred, an attempt was made

to isolate the sulphonic acid by precipitation as the barium salt. It was found impossible to separate this from barium sulphate which was present in bulk. The mixture of barium salts charred on heating, indicating the presence of organic matter.

The 9-fluorenylallylacetic acid was insoluble in the sulphuric acid except when sulphonation occurred.

Phosphoric acid was tried as a cyclisating agent under the conditions described by Bogert and Davidson (J.A.C.S. 1934, 56, 185) and Roblin, Davidson and Bogert (J.A.C.S. 1935, 57, 151).

Phosphoric acid 5 c.c. was heated till it was boiling at over 230°C. 9-Fluorenylallylacetic acid (0·5 g.) was added and the suspension was heated to 230°-250°C for 15 minutes. After cooling, water was added and the solid filtered.

m.p. 120° - 129°C.

Recrystallised from hot water m.p. 126° - 129°C. Mixed m.p. with starting material gave no depression.

Cyclisation was tried using a method similar to the experiment described in Organic Syntheses, 26, 28., but without success.

11 c.c. 90% phosphoric acid and 2·5 c.c. concentrated sulphuric acid were stirred together at -10°C. 0·25 g.

9-Fluorenylallylacetic acid was added and the temperature allowed to rise to 0°-10°C with constant stirring. After 4 hours, the suspension was poured into 50 c.c. water and partly neutralised with 30 c.c. 40% sodium hydroxide with good cooling. An almost quantitative recovery of 9-fluorenylallylacetic acid was obtained.

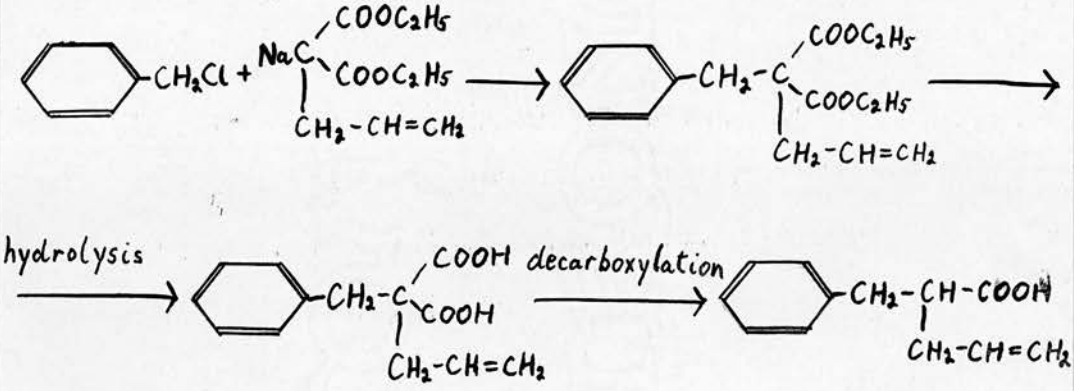
m.p. 121° - 127°C.

Mixed m.p. with 9-fluorenylallylacetic acid gave no depression.

The reaction was repeated at 45° - 50°C, but only unchanged 9-fluorenylallylacetic acid was obtained. As only 0·15 g. could be recovered, it appeared as if some sulphonation had occured.

III. Preparation of 1:2:3:4-tetrahydro-4-methyl-2-naphthoic acid.

1st Stage:- Preparation of allylbenzylacetic acid



This preparation has been described by Johnson and Hill (Am. Chem. Journ., 1911, 45, 364. and Am. Chem. Journ., 1911, 46, 548).

Diethyl allylmalonete (10 g.) was condensed with 6·3 g. benzyl chloride in the presence of 1·15 g. sodium and 20 c.c. absolute alcohol. The resulting oil was distilled under reduced pressure and the fraction 200° - 205° C/40 mm. was collected.

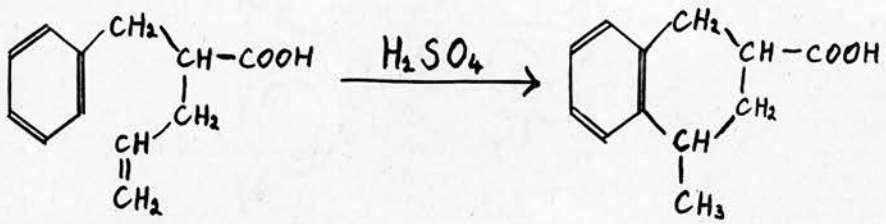
lit. b.p. 228° - 230°/60-65 mm.

Yield 6·0 g. 41%.

5 g. of this oil was hydrolysed by 7 g. of potassium hydroxide in 20 c.c. 50% ethyl alcohol. This solution was refluxed for 14 hours in a water bath, then cooled and acidified with dilute hydrochloric acid and extracted with ether. The ether layer was separated, dried with anhydrous sodium sulphate, and the ether removed, The oil was distilled under reduced pressure, decarboxylation taking place. The fraction 189° - 191° C/40 mm. was collected. The product was a thick viscous colourless oil.

Yield 2·1 g. 61·5%.

2nd Stage:- Preparation of 1:2:3:4-tetrahydro-4-methyl-2-naphthoic acid.



The cyclisation was carried out as described by G. Darzens (Compt. Rend., 1926, 183, 748).

Allylbenzylacetic acid (1 g.) was shaken with 3 g. of 80% sulphuric acid. The 2 liquids were completely miscible. The solution was left in contact with ice for 5 hours. The solution was then neutralised with 12% sodium carbonate solution, extracted with ether, and the ether layer removed. The aqueous layer on acidification gave a white solid which recrystallised from 80% acetic acid. Colourless prisms were obtained.

m.p. 117° - 119°C. (G. Darzens m.p. 121°).

p-nitrobenzylester m.p. 56·5° - 57°C.

The quantity of the p-nitrobenzylester obtained, was too small for analysis.

IV. Preparation of 1:5-dimethylnaphthalene.

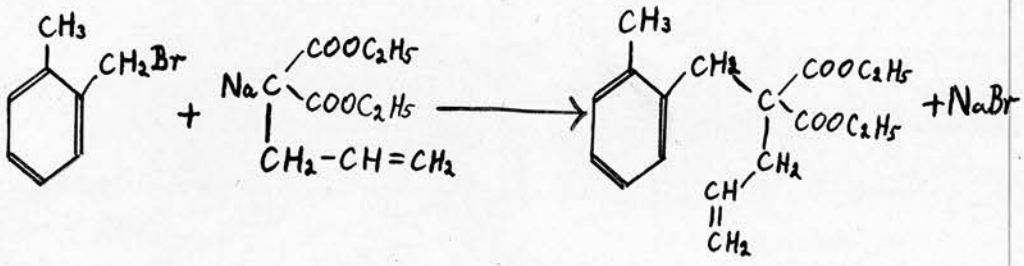
1st Stage:- Preparation of o-methylbenzyl bromide.

The bromination was carried out according to the directions of Atkinson and Thorpe (J.C.S., 1907, 91, 1687).

o-Xylene (50 g.) was brominated with bromine (84 g.) at 130° C. The o-methylbenzyl bromide was distilled and the fraction boiling at 215° - 218° C was collected.

Yield 45 g. 52%.

2nd Stage:- Preparation of diethyl o-xylylallylmalonate.



The malonic ester condensation was carried out in the usual manner. The resulting oil was taken up in ether, dried with anhydrous sodium sulphate and distilled under reduced pressure. The fraction boiling at 199° - 203°C/15 mm. was collected.

From 18 g. o-methylbenzylbromide 10 g. of diethyl o-xylylallylmalonate were obtained.

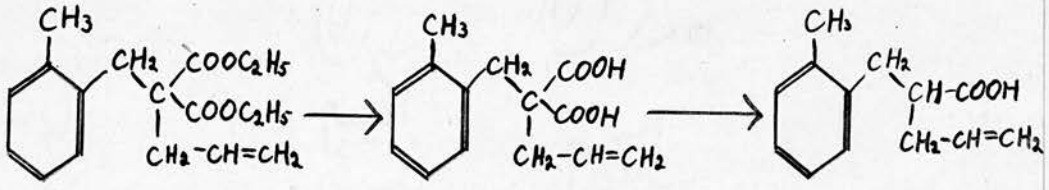
Yield 34%.

Analysis:- fd. C = 70·15% H = 8·12%

$C_{18}H_{24}O_4$ requires

C = 71·01% H = 7·95%

3rd Stage:- Preparation of o-xylylallylacetic acid.



Diethyl o-xylylallylmalonate (6 g.) was hydrolysed by refluxing with potassium hydroxide (8 g.) in 25 c.c. 50% ethyl alcohol. The solution was then acidified with dilute hydrochloric acid, and the oil taken up in ether. The ether layer was separated, dried with anhydrous sodium sulphate, and the ether removed. An oil was obtained which did not solidify in a freezing mixture. It decomposed at 180° C with evolution of carbon dioxide.

The oil was distilled under reduced pressure.

Carbon dioxide was evolved and the fraction boiling at 195° - 200° C/25 mm. was obtained.

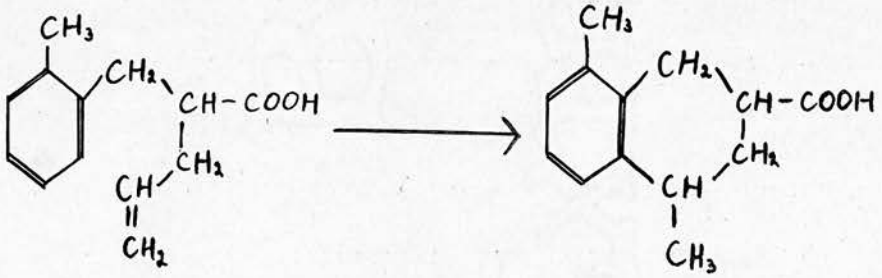
Yield 3 g. 74·5%.

Properties. An alcoholic solution of the acid decolourised aqueous potassium permanganate showing the presence of a double bond.

The acid was soluble in cold aqueous sodium carbonate solution.

o-Xylylallylacetic acid could not be obtained in a pure state since the distillation was accompanied by slight decarboxylation of the monocarboxylic acid.

4th Stage:- Preparation of 1:2:3:4-tetrahydro-4:8-dimethyl-2-naphthoic acid.



o-Xylylallylacetic acid (6 g.) was shaken with 18 g. 80% sulphuric acid in the cold. The solution did not turn clear but remained slightly turbid. A white

solid gradually separated out. After 5 hours, the solution was neutralised with 12% sodium carbonate. The solution was extracted with ether and the ether layer separated. The aqueous layer on acidification yielded a white solid which was recrystallised from 50% ethyl alcohol.

m.p. 141° - 142° C.

Yield 2·0 g. 33%

Analysis:- fd. C = 76·49% H = 7·97%

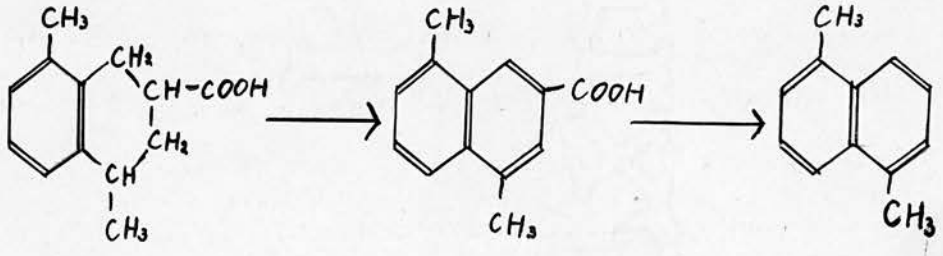
$C_{13}H_{16}O_2$ requires

C = 76·42% H = 7·90%

Properties. The acid was soluble in cold aqueous sodium carbonate solution.

Potassium permanganate was not decolourised by the acid.

5th Stage:- Preparation of 1:5-dimethylnaphthalene.



1 g. 1:2:3:4-tetrahydro-4:8-dimethyl-2-naphthoic acid
2·5 g. chloranil.
10 c.c. xylene.

This mixture was refluxed for 48 hours. The solution was filtered from tetrachlorohydroquinone and an equal volume of ether was added. The naphthoic acid derivative was extracted with 4% potassium hydroxide solution along with some tetrachlorohydroquinone. On acidification of the aqueous layer a brown tar was obtained. This was repeatedly extracted with hot water from which were obtained white plates. Recrystallised from hot water.

m.p. 186° - 188° C.
Yield 2·0 g. 20%

The 4:8-dimethyl-2-naphthoic acid obtained was decarboxylated by heating to 215° - 220° C in quinoline with a little copper bronze. When no more carbon dioxide was evolved, the solution was filtered hot and the filtrate acidified with dilute hydrochloric acid. The 1:5-dimethylnaphthalene crystallised out in white plates. Recrystallised from 50% ethyl alcohol.

m.p. 79° - 80° C. (lit. m.p. 80° C).

Picrate obtained in yellow-orange needles.

m.p. 137° - 139°C. lit. m.p. 138° - 139°C.

An attempt was made to decarboxylate 1:2:3:4-tetrahydro-4:8-dimethyl-2-naphthoic acid under the above conditions but without success. The unchanged acid was obtained.

V. Preparation of 1-(diphenylmethyl)-Δ^3-pentenic acid.

1st Stage:- Preparation of diphenylmethyl bromide.

$$(C_6H_5)_2CH_2 \xrightarrow{Br_2} (C_6H_5)_2CHBr + HBr.$$

The method used was that of Norris, Thomas, Brown (Ber., 1910, 43, 2959).

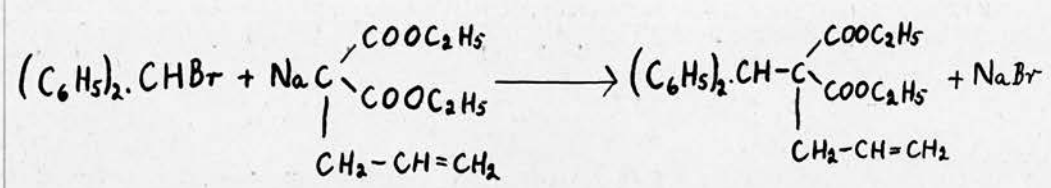
20 g. diphenylmethane.

7 g. bromine.

The bromine was slowly added to the diphenylmethane which was kept at 150° - 160°C. The resulting oil was distilled under reduced pressure and the diphenylmethyl bromide distilled at 179° - 185°C/21 mm. lit. b.p. 184°C/20 mm.

Yield 21·0 g. 71·4%.

2nd Stage:- Preparation of diethyl allyl(diphenylmethyl)-malonate.



22·0 g. diphenylmethyl bromide.

18·0 g. diethyl allylmalonate.

2·12 g. sodium.

60 c.c. absolute alcohol.

The condensation was effected in the usual manner. A pale brown oil was obtained which was distilled under reduced pressure. Some low boiling fractions were obtained which consisted of starting materials. The bulk of the remainder distilled with slight decomposition at 235° - 242°C/26 mm. Redistilled at 237° - 239°C/26 mm. A colourless oil was obtained.

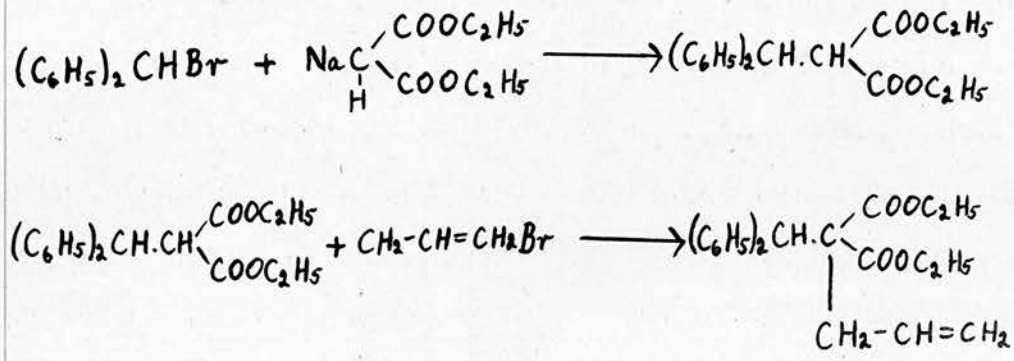
Yield 12·1 g. 37·1%

Analysis:- fd. C = 75·85% H = 7·23%

$C_{23}H_{26}O_4$ requires.

C = 75·37% H = 7·15%

Diethyl allyl(diphenylmethyl)malonate was also prepared by condensing diphenylmethyl bromide with diethyl malonate followed by condensation with allyl bromide



The condensation of diphenylmethyl bromide with diethyl malonate was effected in the normal way and the resulting brown oil distilled under reduced pressure. The fraction 230° - 238°C/27 mm. was collected. Redistilled at 233° - 235°C/27 mm. The oil solidified on standing.

Yield 48·7%

m.p. 43° - 45°C.

Analysis:- fd. C = 73·71% H = 6·92%

$C_{20}H_{22}O_4$ requires

C = 73·60% H = 6·79%

Diethyl (diphenylmethyl)malonate (0·5 g.) was hydrolysed by refluxing for 3 hours with 50 c.c. 30% sodium hydroxide. The solution was acidified and the (diphenylmethyl)malonic acid was filtered off. This was decarboxylated by heating to 170° - 180°C. The residue was recrystallised from aqueous alcohol to give

β-β-diphenylpropionic acid.

m.p. 151° - 153°C. lit. m.p. 155°C.

Anilide m.p. 175° - 177°C. lit. m.p. 177° - 178°C.

$(C_6H_5)_2CH.CH(COOC_2H_5)_2 \xrightarrow{\text{hydrolysis.}} (C_6H_5)_2CH.CH(COOH)_2$

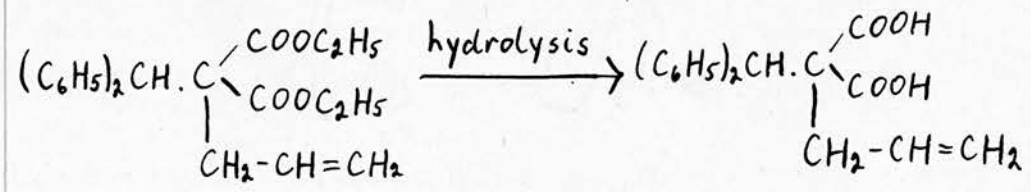
$(C_6H_5)_2CH.CH(COOH)_2 \xrightarrow{\text{decarboxylation}} (C_6H_5)_2CH.CH_2.COOH$

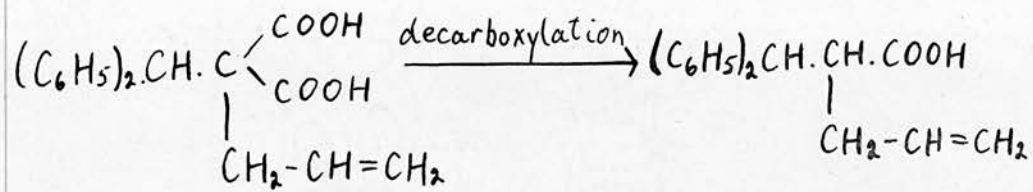
Diethyl (diphenylmethyl)malonate was condensed with allyl bromide in the usual way and the oil distilled under reduced pressure at 236° - 238°C/27 mm.

Yield 39%.

Both samples of diethyl allyl(diphenylmethyl)malonate gave the same acid on hydrolysis and decarboxylation.

3rd Stage:- <u>Preparation of 1-(diphenylmethyl)-Δ^3-pentenic acid</u>.





12 g. diethyl allyl(diphenylmethyl)malonate.

50 c.c. 10% sodium hydroxide.

This mixture was refluxed for 3 hours. The solution was then acidified with dilute hydrochloric acid and white plates were obtained.

m.p. 165° - 170°C with evolution of carbon dioxide.

The solid was heated at 180°C until evolution of gas was complete. The oil was cooled and crystallised from benzene in colourless prisms. A further crop was obtained by adding light petroleum (b.p. 60° - 80°).

m.p. 156° - 157°C.

The compound was soluble in sodium carbonate and decolourised potassium permanganate in the cold.

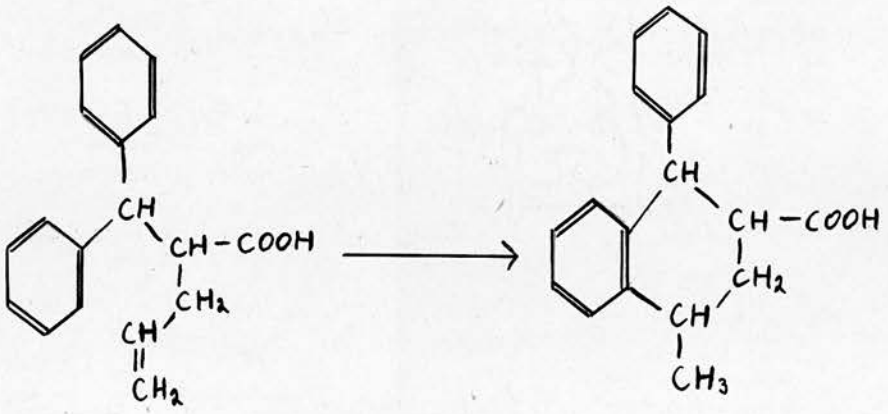
Analysis:- fd. C = 79·82% H = 6·24%

$C_{18}H_{18}O_2$ requires

C = 81·15% H = 6·81%

VI. Attempted cyclisation of 1-(diphenylmethyl)-Δ^3-pentenic acid.

The cyclisation of 1-(diphenylmethyl)-Δ^3-pentenic acid was tried under various conditions in an attempt to form 1:2:3:4-tetrahydro-1-phenyl-4-methyl-2-naphthoic acid.



Sulphuric acid, phosphoric acid and a mixture of these were used as cyclisating agent without success. The following conditions were tried.

Strength of H_2SO_4 (by weight)	Temperature	Time	Result
80%	cold	48 hrs.	Unchanged.
80%	55° - 60°C	4 "	Unchanged.
80%	100°C	4 "	Unchanged.
80%	115° - 125°C	4 "	Charring with sulphonation.
65%	115° - 125°C	4 "	Unchanged.
65%	150° - 160°C	2½ "	Charring.

In every case, the 1-(diphenylmethyl)-Δ^3-pentenic acid was insoluble in the sulphuric acid and the mixture was shaken to form a fine suspension. On dilution and filtration of the solid, it was shown by m.p. and mixed m.p. that no reaction had taken place. Where sulphonation

seemed to have occurred, the solution gradually turned dark. When water was added, only a cloudy solution with some specks of carbon floating in it could be obtained.

The cyclisation was attempted with boiling phosphoric acid for four minutes. Charring occurred rapidly and the brownish solid, which was obtained after dilution, had a m.p. 149° - 154°C.
Mixed m.p. gave no depression.

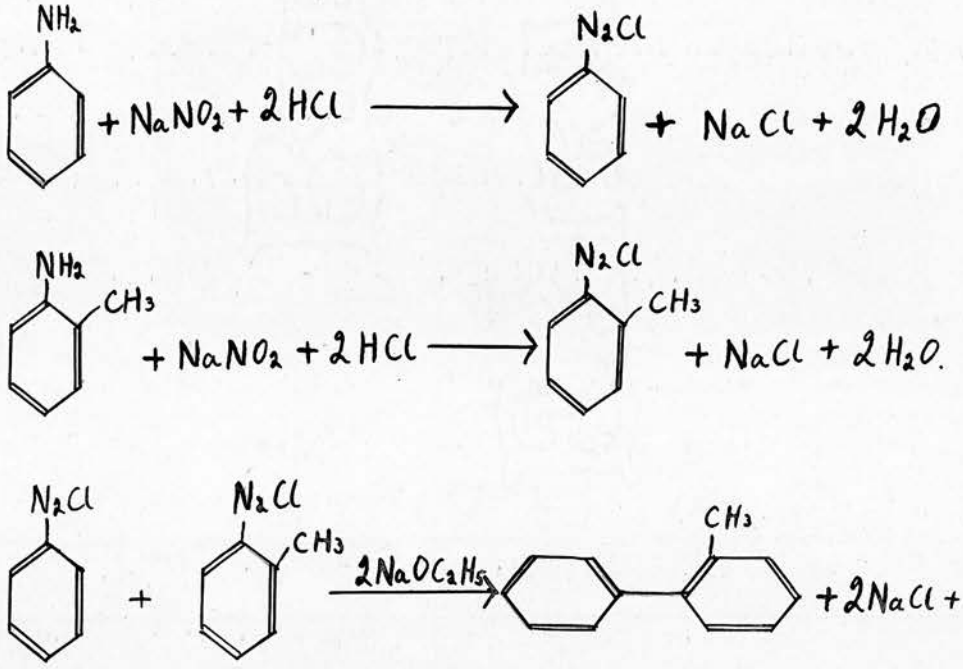
Another attempt was carried out using a 5:1 mixture of phosphoric acid and sulphuric acid at 55° - 60°C for 1 hour. The solution began to char. After cooling and dilution a solid was obtained.

m.p. 152° - 154°C.

Mixed m.p. gave no depression.

VII. Preparation of 2-methyldiphenyl.

An attempt was made to prepare 2-methyldiphenyl by diazotising an equimolecular mixture of aniline and o-toluidine followed by coupling with sodium ethoxide ——Oddo and Curatolo (Gaz. Chim. Ital., 1895, 25, 126). This method proved unsatisfactory as only a small yield was obtained.



18·6 g. aniline (1 equiv.)
21·4 g. o-toluidine (1 equiv.)
24·2 g. (26 c.c.) concentrated hydrochloric acid (4 equivs.)
27·6 g. sodium nitrite (2 equivs.)

The amines were diazotised in the minimum amount of water, the temperature being kept below 10°C. This mixture was added with stirring in small amounts to 15 g. sodium dissolved in 150 c.c. absolute alcohol. After the solution had been refluxed on the steam bath for ½ hour, the solution was steam distilled and 2 l. of distillate collected. The distillate was extracted with ether, and the ether layer dried and distilled under reduced pressure. The fraction distilling at 135° - 140°C/25 mm. amounted to 0·5 g.

lit. b.p. 130° - 136°C/27 mm.

2-methyldiphenyl was prepared by coupling o-bromotoluene and cyclohexanone by means of a Grignard reaction to form 1-o-tolylcyclohexanol followed by dehydration and dehydrogenation. These operations were carried out in a number of stages which are described below.

1st Stage:- Preparation of o-bromotoluene.

The conditions of this reaction are given by Bigelow (Org. Synth., 1929, 9, 22).

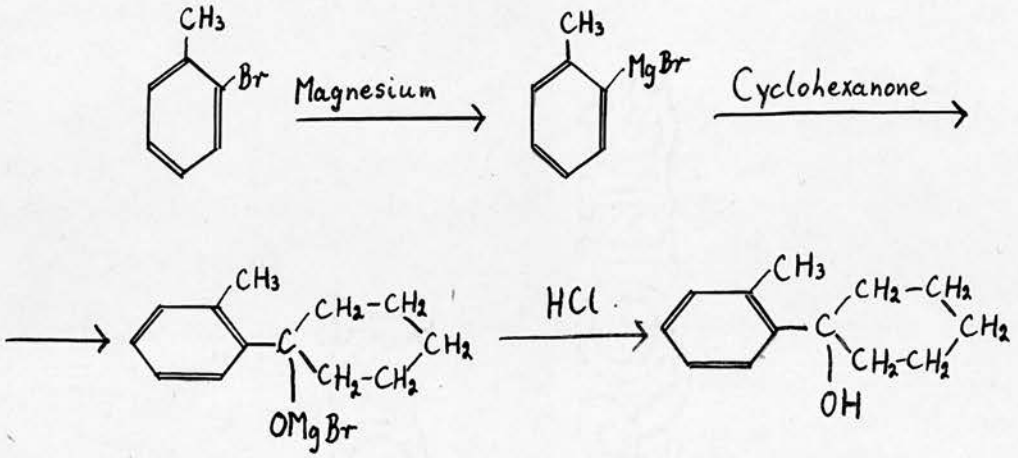
128 g.	o-toluidine
800 c.c.	35% hydrobromic acid
92 g.	sodium nitrite
4 g.	copper bronze

The o-toluidine on diazotisation and decomposition gave o-bromotoluene which was distilled.

b.p. 178° - 181°C. lit. b.p. 181°C.

Yield 50 g. 25%.

2nd Stage:- Preparation of 1-o-tolylcyclohexanol.



The reaction was carried out according to directions of Sherwood, Short and Stansfield. (J.C.S., 1932, 1832) and Orchin (J.A.C.S., 1945, 67, 499).

55 g.	o-bromotoluene
7·5 g.	magnesium turnings
31 g.	cyclohexanone in 30 c.c. anhydrous ether
220 c.c.	anhydrous ether.

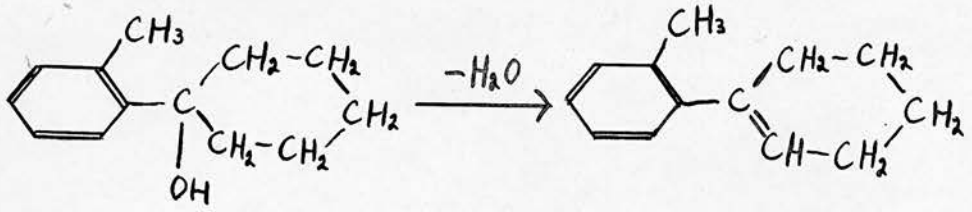
The magnesium was placed in a flask fitted with a dropping funnel, and a reflux condenser with a calcium chloride tube. Ether (30 c.c.) was added and moist air was expelled by warming. The o-bromotoluene was mixed with the rest of the ether and a little added to the magnesium. The reaction was started by the addition of a few drops of methyl iodide. The rest of the o-bromotoluene in ether was added slowly. The solution

was refluxed for 1½ hours until all the magnesium dissolved. The cyclohexanone was now added slowly, and the solution refluxed for 24 hours. The solution was cooled, and crushed ice was added to decompose the white condensation product. Dilute hydrochloric acid was added to dissolve the magnesium hydroxide. The ether layer was separated, dried with anhydrous sodium sulphate, and distilled under reduced pressure. The fraction distilling at 154° - 6°C/25 mm. was collected.

Yield 38 g. 62%

b.p. 154° - 6°C/25 mm. lit. b.p. 149° - 151°C/14 mm.

3rd Stage:- <u>Preparation of o-tolyl-Δ^1-cyclohexene</u>.



25 g. 1-o-tolylcyclohexanol.

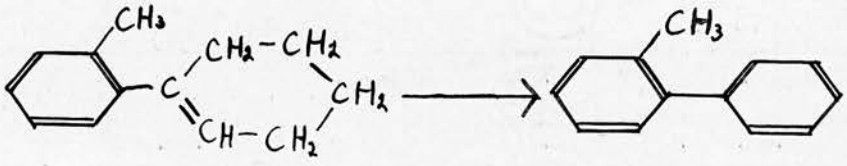
25 c.c. 90% formic acid.

This mixture was shaken in the cold. After a few

seconds, the solution turned cloudy and the hydrocarbon separated out. After ½ hour, the hydrocarbon layer was separated, washed with sodium hydroxide, water and dried with calcium chloride.

Yield 22 g. 97%.

4th Stage:- Preparation of 2-methyldiphenyl.



20 g. o-tolyl-Δ^1-cyclohexene.
57·5 g. chloranil.
150 c.c. xylene.

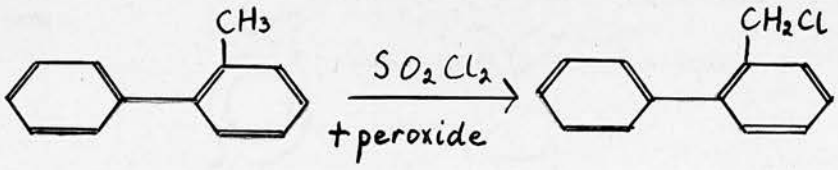
This mixture was refluxed for 24 hours. When cold the solution was filtered from tetrachlorohydroquinone. An equal volume of ether was added to the filtrate.

The filtrate was washed twice with 4% potassium hydroxide, then water, dried and fractionated under reduced pressure.

b.p. 134° - 141°C/25 mm. lit. b.p. 130°-136°C/27 mm.

Yield 12 g. 61·5%.

VIII Attempted chlorination of 2-methyldiphenyl.



3·36 g. 2-methyldiphenyl.

2·70 g. sulphuryl chloride.

0·23 g. benzoyl peroxide.

This mixture was first warmed gently and then refluxed for 1½ hours with an efficient condenser. The solution was then fractionated under reduced pressure and the following fractions obtained.

135° - 142°C/24 mm. --- 1·1 g. of colourless oil which consisted mainly of 2-methyldiphenyl. No chlorine was found in this fraction.

143° - 155°C/24 mm. --- 0·5 g. of slightly yellow oil which contained chlorine and which was sent away for analysis.

b.p. of o-phenylbenzyl chloride is 154°C/12 mm.

Analysis of fraction 143° - 155°/24 mm.

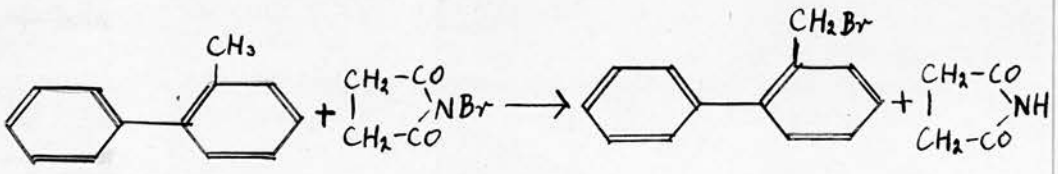
fd. Cl = 8·79%

$C_{13}H_{11}Cl$ requires Cl = 17·49%

It thus appeared as if the reaction had only gone

partially.

IX. Preparation of o-phenylbenzyl bromide.



3·5 g. 2-methyldiphenyl

4·5 g. N-bromosuccinimide

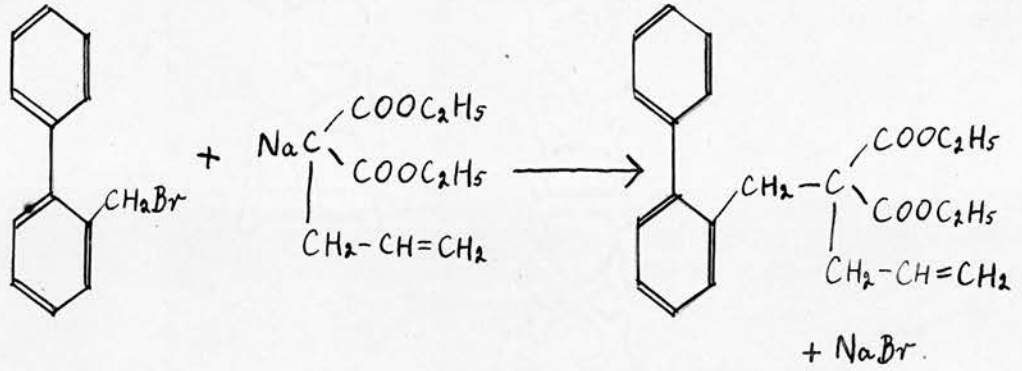
20 c.c. carbon tetrachloride

This mixture was refluxed for 3 hours. The solution was cooled, filtered, and distilled under reduced pressure at 168° - 172° C/18 mm.

lit. b.p. 166°C/12 mm.

Yield 4·13 g. 80%.

X Preparation of diethyl allyl(o-phenylbenzyl)malonate.



5·75 g. o-phenylbenzyl bromide

4·60 g. diethyl allylmalonate

0·54 g. sodium

10 c.c. absolute alcohol

The condensation was carried out in the usual way. The resulting oil was distilled under reduced pressure and the fraction b.p. 240° - 265°C/23 mm. was collected. The distillate solidified and was recrystallised from light petroleum (b.p. 40° - 60°) in colourless needles.

m.p. 68° - 69°C.

Yield 3·53 g. 41%

Analysis: fd. C = 75·29% H = 7·39%

$C_{23}H_{26}O_4$ requires C = 75·37% H = 7·15%

XI Hydrolysis of diethyl allyl(o-phenylbenzyl)malonate.

(a) Diethyl allyl(o-phenylbenzyl)malonate (1 g.) was refluxed with 10 c.c. 10% sodium hydroxide for 16 hours. On cooling, a white solid was obtained which was shown by m.p. and mixed m.p. to be unchanged ester.

(b) The ester (2·0 g.) was refluxed for 3 hours with 25 c.c. 10% alcoholic sodium hydroxide. The solution was cooled, acidified with dilute hydrochloric acid, extracted with ether, washed, dried and evaporated to dryness. A brown oil resulted which could not be

crystallised nor distilled under reduced pressure without decomposition.

This oil was decarboxylated by heating to 180°C until no more carbon dioxide was evolved. An oil was obtained which could not be crystallised, distilled under reduced pressure nor purified.

(c) The ester (1·0 g.) was dissolved in and refluxed with a mixture of 5 c.c. 50% sulphuric acid and 15 c.c. glacial acetic acid for 2 hours. The solution was worked up as in the previous experiment. An oil was obtained which behaved as before.

XII Attempted cyclisation of diethyl allyl(o-phenylbenzyl)malonate.

The following conditions were tried, but no cyclisation occurred.

Strength of H_2SO_4 (by weight)	Temperature	Time	Result
65%	cold	48 hrs.	Unchanged
65%	75° - 80°C	4 "	Unchanged
65%	100°C	4 "	Unchanged
65%	120° - 125°C	2 "	Charring
80%	cold	48 "	Unchanged
80%	75° - 80°C	2 "	Unchanged with charring
80%	100°C	5 mins.	Charred.

XIII Preparation of ethyl o-phenylbenzoate.

1st Stage:- Preparation of diphenyl-2-carboxylic acid.

The reaction was carried out according to the directions of Graebe and Rateanu (Ann., 1894, 279, 257).

Fluorenone (40 g.) was fused with potassium hydroxide (120 g.) and water (2 c.c.) at 180° - 200°C. On acidification, diphenyl-2-carboxylic acid was obtained. Crystallised from light petroleum (b.p. 60° - 80°).

m.p. 112° - 113°C. lit. m.p. 114°C.

Yield 33·5 g. 76%

o-phenylbenzoyl chloride was prepared by heating 2·0 g. diphenyl-2-carboxylic acid with 1·2 g. thionyl chloride under reflux for 1 hour. The black oil was distilled under reduced pressure and a yellow oil was obtained.

b.p. 163° - 6°C/12 mm. lit. b.p. 169°C/16mm.

Yield 1·1 g. 50%

o-phenylbenzamide was prepared by shaking 0·5 g. o-phenylbenzoyl chloride with 10 c.c. concentrated ammonia. The amide was filtered, washed with ether and sodium carbonate solution, and recrystallised from 50% alcohol in colourless needles.

m.p. 176° - 177°C. lit. m.p. 177°C.

2nd Stage:- Preparation of ethyl o-phenylbenzoate.

5 g. diphenyl-2-carboxylic acid

15 c.c. alcohol

0·5 c.c. concentrated sulphuric acid.

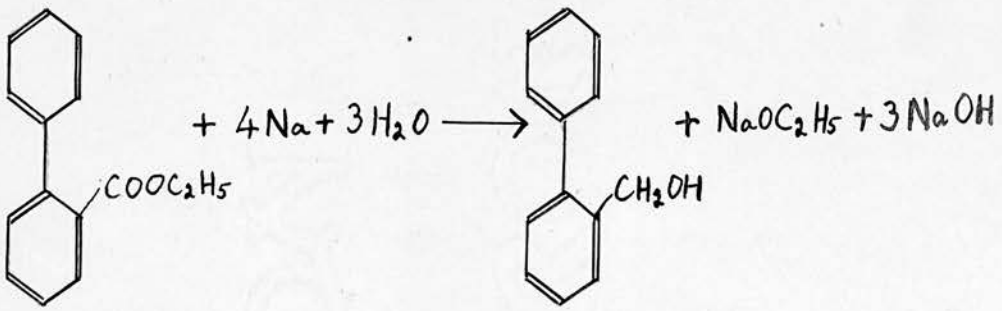
This mixture was refluxed for 8 hours. Most of the alcohol was then distilled off from a water bath, and the residue poured into water. The ester was taken up in ether and washed with sodium carbonate solution. The ether layer was dried over anhydrous sodium sulphate and distilled under reduced pressure.

b.p. 163° - 4°C/9 mm. lit. b.p. 163° - 6°C/12mm.

Yield 4·5 g. 78·5%

XIV Attempted reduction of ethyl o-phenylbenzoate.

An attempt to reduce ethyl o-phenylbenzoate by the Prins modification of the Bouveault and Blanc method (Rec. Trav. Chim., 1923, 42, 1050) proved unsuccessful. The equation of the proposed reaction is



4·5 g. ethyl o-phenylbenzoate.
15 g. ether.
5 c.c. saturated sodium acetate solution.
3 g. sodium.

The ester was dissolved in the ether and the sodium acetate solution added to form a bottom layer. A stirrer was arranged so that only the ether layer was slowly stirred. The whole solution was kept at -10°C - 0°C.

The sodium was gradually added in small pieces, the whole addition taking four days. The ether layer was kept neutral or slightly acid to prevent hydrolysis by the addition of 30% acetic acid. Only small bubbles of hydrogen appeared. The ether layer was separated, dried with anhydrous sodium sulphate, and distilled under reduced pressure. The bulk of the solution distilled at 160° - 170°C/13 mm. lit. b.p. of o-phenylbenzyl alcohol 174°C/13 mm.

Yield 2·0 g.

The bulk of this oil proved to be unchanged ester as, on hydrolysis with 20 c.c. 30% sodium hydroxide for 5 hours, most of the oil dissolved. A small quantity of oil remained and this was separated, washed and dried. It was converted into a p-nitrobenzoate. Crystallised from alcohol.

m.p. 235° - 237°C.

This was not p-nitrobenzoic acid m.p. 238°C as a mixed m.p. gave a depression.

Analysis: fd. N = 5·93%.

As the p-nitrobenzoate of o-phenylbenzyl alcohol ($C_{20}H_{15}O_4N$) required N = 4·20%, it seemed reasonable to suppose that this was the desired compound but slightly impure.

XV Preparation of o-bromobenzonitrile.

1st Stage:- Preparation of o-bromobenzoyl chloride.

25 g. o-bromobenzoic acid.
16 g. thionyl chloride.

This mixture was heated under reflux in a water bath for 1½ hours. The solid gradually turned into an oil and sulphur dioxide and hydrogen chloride were given off. The oil was distilled under reduced pressure.

b.p. 124° - 128°C/20 mm. lit. b.p. 125°C/20 mm.

Yield 25 g. 91·5%.

2nd Stage:- Preparation of o-bromobenzamide.

25 g. o-bromobenzoyl chloride was mixed with 25 c.c.

ether and the solution saturated with dry ammonia gas. The ammonium chloride and the amide were filtered off. More ammonia was passed into the filtrate. In this way 4 crops of o-bromobenzamide were obtained. The precipitate was well washed with water to dissolve the ammonium chloride.

m.p. 155° - 156°C. lit. m.p. 156°C.
Yield 20 g. 88%.

3rd Stage:- Preparation of o-bromobenzonitrile.

16 g. o-bromobenzamide (1 equiv.)
6 g. phosphorus oxychloride (½ equiv.)

The mixture was heated under reflux in a water bath. The solid dissolved and bubbles of hydrogen chloride appeared. The heating was stopped when no more hydrogen chloride was evolved. The liquid on cooling crystallised out. The solid was shaken with water to dissolve the phosphorus oxychloride and the nitrile extracted with ether. The ether layer was dried with anhydrous sodium sulphate and the ether allowed to evaporate. White needles were obtained which were re-crystallised from alcohol.

m.p. 53°C. lit. m.p. 53°C.

Yield 12·5 g. 86%.

XVI Ullmann Reaction on o-bromobenzonitrile and iodobenzene.

3·6 g.	o-bromobenzonitrile.
4 g.	iodobenzene.
7 g.	copper bronze.
10 c.c.	nitrobenzene.

This mixture was heated in an oil bath at 195° - 205°C for 5 hours with an air reflux condenser. The mixture was then filtered hot through a sintered glass crucible and the insoluble residue washed with acetone. The acetone was added to the filtrate. The mixture was steam distilled to remove nitrobenzene and acetone. The oil was extracted with ether, the ether layer separated, and dried with anhydrous sodium sulphate. When the ether was taken off a black oily solid was obtained. This solid could not be purified by trituration or by chromotographic adsorption. The solid was soluble in benzene, alcohol and ether; insoluble in light petroleum.

XVII Preparation of 2:2′-dimethyldiphenyl.

1st Stage:- Preparation of o-iodotoluene.

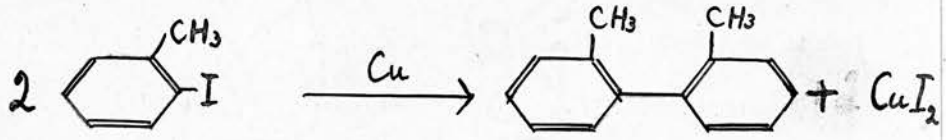
o-Iodotoluene was prepared by the method of Griess (Ann., 1866, 137, 76).

50 g.	o-toluidine.
100 g.	(54 c.c.) concentrated sulphuric acid in 500 c.c. water.
40 g.	sodium nitrite in 80 c.c. water.
60 g.	potassium iodide in 200 c.c. water.

The o-toluidine was diazotised and decomposed. A black oil was obtained. Free iodine was removed by shaking with sodium bisulphite. The oil was dried over anhydrous sodium sulphate and distilled at 205° - 210°C/ 750 mm. lit. b.p. 207°C/726 mm.

Yield 55 g. 54%.

2nd Stage:- Preparation of 2:2′-dimethyldiphenyl.



This reaction has been carried out by Ullmann (Ann., 1904, 332, 38). Ullmann heated equal weights of o-iodotoluene and copper bronze together in a sealed tube at

230°C for 3 hours. It was found, however, that under these conditions, very little 2:2′-dimethyldiphenyl was formed, the bulk of the product consisting of unchanged o-iodotoluene. When the temperature was raised 50°C the reaction proceeded and the best results were obtained with the following conditions.

10·5 g. o-iodotoluene.
10·5 g. copper bronze.

The mixture was heated in a sealed tube in an oven at 280°C for 6 hours. The semi-solid reaction product was extracted with ether, filtered and distilled.

The oil distilled at 251° - 258°C/747 mm. The distillate solidified in a freezing mixture.

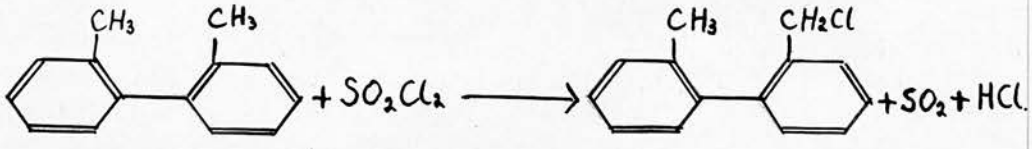
m.p. 13° - 18°C. lit. m.p. 18°C.
Yield 2·7 g. 62%.

2:2′-dimethyldiphenyl could not be prepared from o-bromotoluene under the above conditions even when the time of heating was increased to 15 hours. Nearly all the o-bromotoluene was recovered unchanged.

Oxidation of 2:2′-dimethyldiphenyl with aqueous potassium permanganate gave diphenic acid m.p. 226°-228°C. lit. m.p. 228°C.

XVIII Attempted chlorination of 2:2′-dimethyldiphenyl.

An attempt to prepare 2-methyl-2′-chloromethyl-diphenyl by chlorination of 2:2′-dimethyldiphenyl according to the following equation proved unsuccessful.



2·0 g. 2:2′-dimethyldiphenyl.

1·53 g. sulphuryl chloride.

0·13 g. benzoyl peroxide.

This mixture was warmed for 1½ hours under reflux. The black oil was distilled at 132° - 138°C/25 mm. The distillate consisted of a brown oil which partly solidified in a freezing mixture and the colourless needles filtered off.

m.p. 12° - 17°C.

2:2′-dimethyldiphenyl m.p. 18°C.

The oil was analysed.

Analysis: fd. Cl = 6·84%.

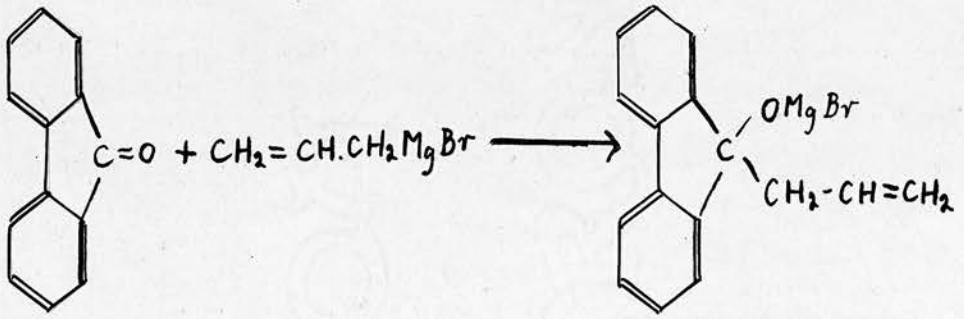
$C_{14}H_{13}Cl$ requires Cl = 16·38%.

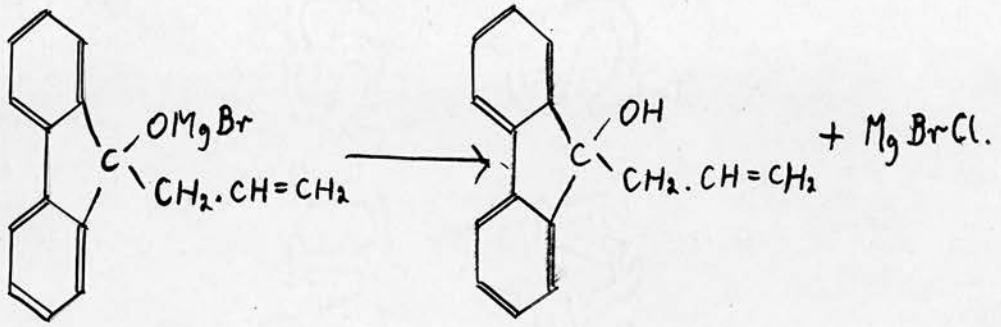
This indicated that the chlorination had only proceeded partially.

(B) CYCLODEHYDRATION OF EPOXIDE

XIX Preparation of 9-allyl-9-hydroxyfluorene.

Allyl magnesium bromide has been successfully prepared by Gilman and McGlumphy (Bull. Soc. Chim., 1928, 43, 1322) using freshly powdered magnesium. A number of Grignard reactions involving the use of allyl magnesium bromide have been carried out by them and also by Allan and Henz (J.A.C.S., 1939, 61, 1790). It was hoped to prepare 9-allyl-9-hydroxyfluorene by a Grignard reaction on fluorenone and allyl magnesium bromide. This reaction has been carried out by Backer and Strating (Rec. Trav. Chim., 1941, 60, 391).





Unfortunately, the only magnesium available was coarse magnesium turnings. This was found to be unsuitable as allyl magnesium bromide readily reacts with allyl bromide to form diallyl. Thus the magnesium has to compete with allyl magnesium bromide for the allyl bromide.

$$CH_2=CH.CH_2MgBr + CH_2=CH.CH_2Br \longrightarrow CH_2=CH.CH_2.CH_2.CH=CH_2 + MgBr_2$$

5 g. magnesium turnings (0·2 moles).

11.9 g. allyl bromide (0·1 moles).

385 c.c. anhydrous ether. (3·75 moles).

14·4 g. fluorenone in 250 c.c. ether (0·08 moles).

The magnesium and 25 c.c. ether were placed in a flask fitted with a mercury seal stirrer, dropping funnel and a water condenser. The rest of the ether was mixed with the allyl bromide and slowly added with constant and vigorous stirring. The flask warmed slightly and part of the magnesium reacted. The whole addition took 1 hour. The solution was quickly filtered from the excess magnesium and was cooled in ice. The fluorenone, dissolved in ether, was slowly added and the mixture allowed to stand overnight. An orange precipitate formed. Ice was then added, the solution acidified with dilute sulphuric acid and the ether layer separated and

dried. The ether was distilled off and yellow needles of fluorenone were obtained (shown by m.p. and mixed m.p.)

m.p. 81° - 82°C. lit. m.p. 84°C.

The solid was taken up in benzene and passed through a column of alumina but only fluorenone was obtained. 12·5 g. fluorenone was recovered.

The above procedure was repeated using benzophenone instead of fluorenone in an attempt to repeat the work of Gilman and McGlumphy (Bull. Soc. Chim., 1928, 43, 1322). Only benzophenone could be recovered from the reaction product. It thus appeared that the formation of allyl magnesium bromide is dependent on the type of magnesium used.

9-Allyl-9-hydroxyfluorene was successfully prepared from allyl magnesium chloride. Kharasch and Fuch (J. Org. Chem., 1944, 9, 359) have described the preparation of allyl magnesium chloride and in many cases have found it more satisfactory than allyl magnesium bromide as a Grignard reagent.

$$CH_2=CH.CH_2Cl + Mg \longrightarrow CH_2=CH.CH_2MgCl.$$

1·6 g. magnesium turnings.

4·6 g. allyl chloride.

9·0 g. fluorenone.

The magnesium was placed in a 3 necked flask fitted with an efficient stirrer, a reflux condenser and a dropping funnel. The reflux condenser was connected through a drying tube to a water bubbler. 8 c.c. of anhydrous ether were added to the flask which was cooled in an ice bath. The contents were now vigorously stirred while the allyl chloride mixed with 8 c.c. anhydrous ether was slowly added. The addition was at such a rate that very little gas was evolved. The formation of the Grignard agent was complete in 7 hours. The fluorenone in 200 c.c. anhydrous ether was now slowly added with stirring. The solution was refluxed for 4 hours. The contents, after cooling, were poured onto ice. The solution was acidified with dilute hydrochloric acid and the ether layer separated, washed and dried. On evaporating to dryness a yellow compound was obtained. The solid crystallised from light petroleum (b.p. 60° - 80°) in magnificent pale yellow prisms.

m.p. 114°C. lit. m.p. 119·5° - 120°C.

Yield 5·25 g. 39%.

Analysis: fd. C = 86·02% H = 6·26%.

Calc. for $C_{16}H_{14}O$ C = 86·44% H = 6·35%.

The allyl chloride used was prepared from allyl

alcohol by the method of Coffey and Ward (J.C.S., 1921, 119, 1301)

$$CH_2{=}CH.CH_2OH + HCl \xrightarrow{ZnCl_2} CH_2{=}CH.CH_2Cl + H_2O.$$

Allyl alcohol (46 g.) and anhydrous zinc chloride (20 g.) gave a product which on distillation yielded allyl chloride with some diallyl ether (b.p. 90° - 95°).

b.p. 44° - 47°C. lit. b.p. 45°C.

Yield 22·5 g. 38%.

XX Preparation of 9-hydroxyfluorene-9-allylepoxide.

9-Allyl-9-hydroxyfluorene was oxidised by a chloroform solution of perbenzoic acid, which was prepared according to the directions of von Braun (Org. Synth., 13, 86).

$$(C_6H_5CO)_2O + CH_3ONa \longrightarrow C_6H_5COOONa + C_6H_5COOCH_3$$

$$C_6H_5COOONa + H_2SO_4 \longrightarrow C_6H_5COOOH + NaHSO_4$$

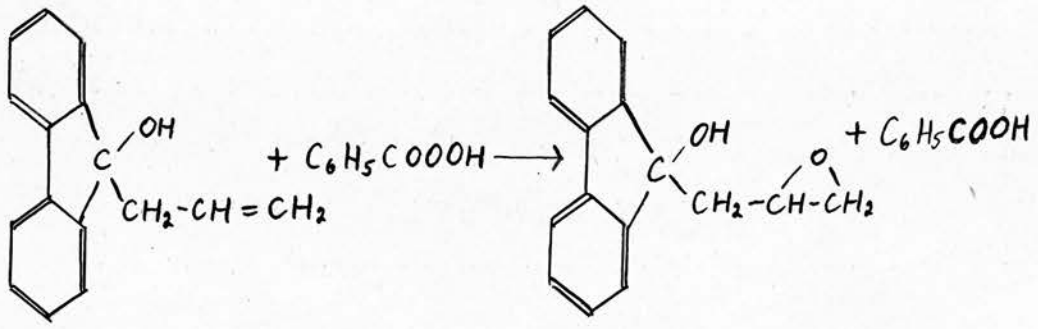
25 g. benzoyl peroxide (0·105 moles).
2·6 g. sodium (0·11 moles).
50 c.c. absolute methyl alcohol.
112 c.c. N. sulphuric acid.

The benzoyl peroxide was dissolved in chloroform

and added to the solution of sodium in methyl alcohol, keeping the temperature below 0°C. The sodium perbenzoate was extracted with water and the acid was liberated by the addition of the sulphuric acid. The perbenzoic acid was extracted with chloroform and washed with water.

Yield 12·4 g. 75·8%. (by iodometric titration).

This chloroform solution was used to prepare 9-hydroxy-fluorene-9-allylepoxide. The method is similar to the procedure of Bradsher and Amore (J.A.C.S., 1943, 65, 2016) who applied it to analogous compounds.



2·22 g. 9-allyl-9-hydroxyfluorene

1·65 g. perbenzoic acid in chloroform.

The 9-allyl-9-hydroxyfluorene was dissolved in the chloroform solution of the perbenzoic acid and left stoppered in the refrigerator. After 24 hours, the

solution was shaken with sodium carbonate solution to remove the acids, and the chloroform layer washed with water. The chloroform layer was separated, dried with anhydrous sodium sulphate, and evaporated to dryness. A yellowish solid was left which was crystallised twice by dissolving in the minimum quantity of benzene and adding twice the volume of light petroleum (b.p. 60° - 80°). Colourless prisms slowly formed.

m.p. 127° - 128°C.

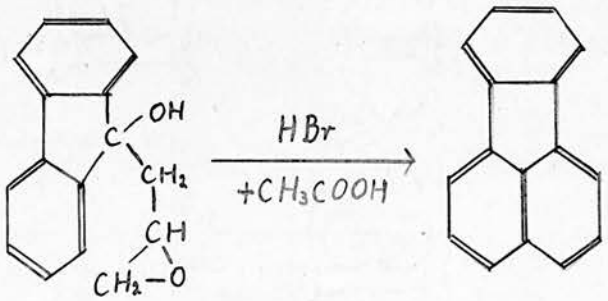
Yield 1·82 g. 76·5%.

Analysis: fd. C = 80·20% H = 5·99%

$C_{16}H_{14}O_2$ requires C = 80·64% H = 5·92%.

XXI Attempted cyclisation of 9-hydroxyfluorene-9-allylepoxide.

The cyclisation was attempted under conditions similar to that carried out by Bradsher and Amore (J.A.C.S., 1943, 65, 2016) on related compounds. The proposed reaction was



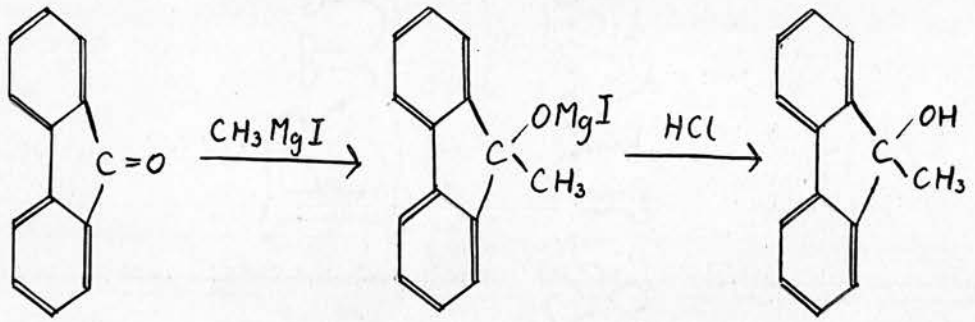
1·6 g. 9-hydroxyfluorene-9-allylepoxide.
16 c.c. glacial acetic acid
11 c.c. 34% hydrobromic acid.

The epoxide was dissolved in the glacial acetic acid and the hydrobromic acid added in the cold. The solution was quite clear. When warmed, the solution quickly turned cloudy and an oil settled which on continued refluxing gave a black brittle resin. The solution was refluxed for 3 days. No fluorescence was observed under the ultra-violet lamp. The solution was poured into water and the resin separated. This solid was dissolved in benzene and passed through a column of alumina and 2 black zones were obtained. Both yielded a black brittle resin which decomposed at over 200°C. It thus appeared as if polymerisation had occurred.

(C) DIELS-ALDER SYNTHESES

XXII Synthesis of fluoranthene.

1st Stage:- Preparation of 9-methyl-9-hydroxyfluorene.



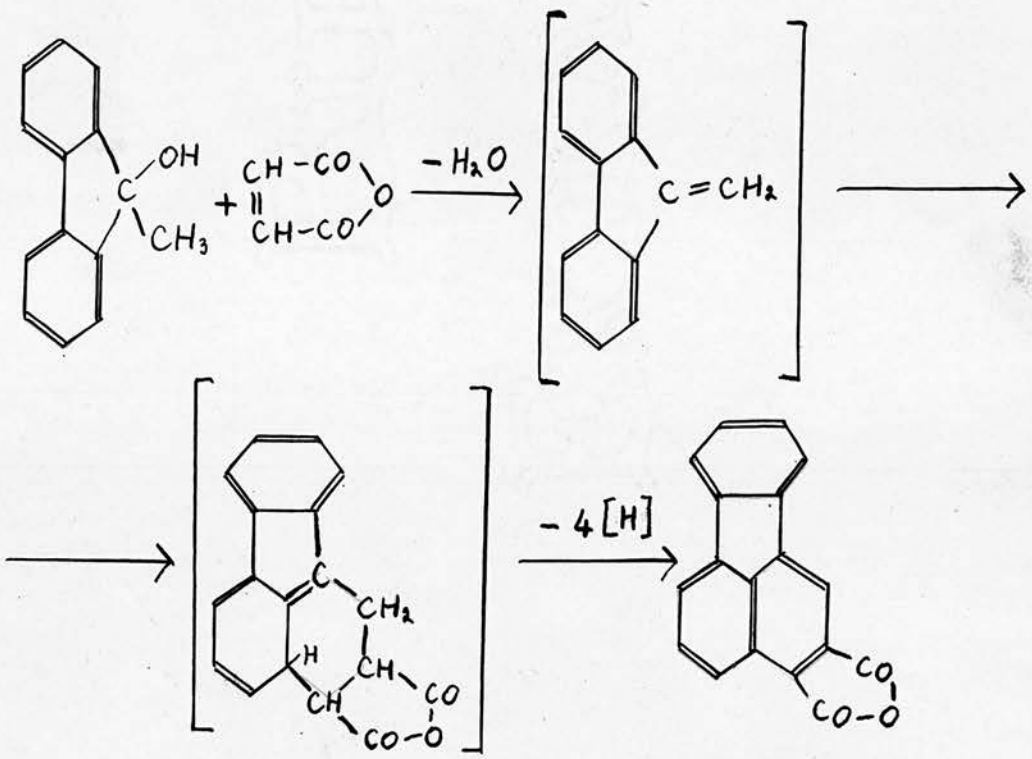
The reaction was carried out following the procedure of Daufresne (Bul. Soc. Chim., 1907, (4) 1, 1233).

3·0 g. magnesium powder.
22·5 g. methyl iodide.
18·75 g. fluorenone.

After the addition of the fluorenone to the Grignard reagent, the solution was refluxed for 20 minutes. The solution was poured onto ice, acidified and washed. The 9-methyl-9-hydroxyfluorene was recrystallised from benzene.

m.p. 174° - 5°C. lit. m.p. 173°C.
Yield 14·43 g. 72%.

2nd Stage:- Preparation of fluoranthene-3:4-dicarboxylic acid anhydride.



12·0 g. 9-methyl-9-hydroxyfluorene.

30 g. maleic anhydride.

80 c.c. acetic anhydride.

This solution was refluxed for 2 hours. The orange-fluorescent solution was cooled and filtered. A yellow crystalline solid was obtained which crystallised from acetic anhydride in yellow needles. The reaction was accompanied by dehydrogenation.

m.p. 267° - 8° C.

Yield 1·60 g. 10%.

Analysis: fd. C = 79·23% H = 3·33%.

$C_{18}H_8O_3$ requires C = 79·43% H = 2·96%.

The yield could not be increased by using nitrobenzene as solvent.

Dimethyl ester - colourless needles from methyl alcohol.

m.p. 118° - 119°C.

Analysis: fd. C = 75·00% H = 4·29%.

$C_{20}H_{14}O_4$ requires C = 75·40% H = 4·43%.

The filtrate from the condensation, on cautious addition of water, gave a pale yellow solid which was recrystallised from glacial acetic acid as an amorphous white powder. It was insoluble in boiling sodium hydroxide, alcohol and light petroleum. Soluble in hot acetic acid and hot benzene.

m.p. 222° - 4°C. (with decomposition).

Analysis: fd. C = 80·91%. H = 5·11%.

It appeared to be a polymer of unknown constitution.

An attempt at condensation by fusion of 9-methyl-9-hydroxyfluorene with excess maleic anhydride at 155° - 165°C for 3 hours gave a pale brown mass which was crystallised from glacial acetic acid as an amorphous white powder. It was insoluble in boiling sodium hydroxide,

sparingly soluble in alcohol, ether and benzene.

m.p. 288° - 290°C(with decomposition).

This also appeared to be a polymer.

Analysis: fd. C = 79·28% H = 5·04%.

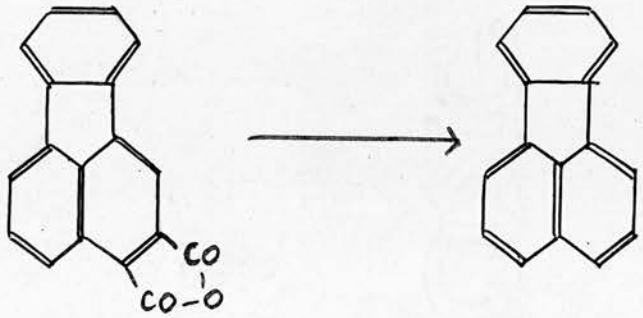
Fluoranthene-3:4-dicarboxylic acid anhydride was soluble in warm sodium carbonate and sodium hydroxide. The solution showed a marked pale blue fluorescence in ultra violet light. On acidification of the alkaline solution, a pale yellow gelatinous precipitate was obtained which also had a pale blue fluorescence. The fluoranthene-3:4-dicarboxylic acid obtained readily reverted to the anhydride in organic solvents so that it could not be recrystallised. The anhydride was obtained from each attempt.

m.p. 267° - 8°C.

Mixed m.p. showed no depression.

When a m.p. of the crude fluoranthene-3:4-decarboxylic acid was tried, the solid deepened in colour at 140° - 160°C to give a bright yellow compound which had an orange fluorescence. It finally melted at 266°- 8°C.

3rd Stage:- Preparation of fluoranthene.



0·5 g. fluoranthene-3:4-dicarboxylic acid anhydride was mixed intimately with 10 times its bulk of calcium hydroxide and heated to red heat in a pyrex tube clamped in a horizontal position. Decarboxylation occurred and fluoranthene sublimed along the tube. The orange solid crystallised from alcohol in colourless needles. Warm sulphuric acid gave a green-blue solution.

m.p. 109° - 110°C. lit. m.p. 110°C.

Mixed m.p. gave no depression.

Picrate-orange needles m.p. 184° - 186°C. lit. m.p. 186°C.

Mixed m.p. gave no depression.

Decarboxylation with quinoline and copper bronze gave a monocarboxylic acid.

0·4 g. fluoranthene-3:4-dicarboxylic acid anhydride.

20 c.c. quinoline.

0·1 g. copper bronze.

This solution was heated in an oil bath at 180°C for ½ hour. Bubbles of carbon dioxide were evolved. The copper bronze was removed by filtration and 10 c.c. 10% sodium hydroxide added to the filtrate. The solution was steam distilled to remove the quinoline. The remaining solution was acidified and the brown gelatinous precipitate crystallised from benzene and light petroleum (b.p. 60° - 80°) to give a pale yellow gelatinous precipitate.

m.p. 240° - 3°C. softened at 237°C.

Analysis: fd. C = 81·10% H = 3·81%

$C_{17}H_{10}O_2$ requires C = 82·90% H = 4·09%.

The acid fluoresced pale blue in ultra violet light. It sublimed slowly at 220°C forming pale yellow needles.

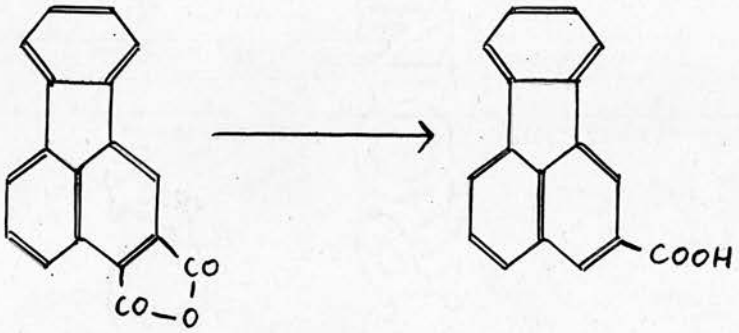
Methyl ester - pale yellow needles from methyl alcohol. m.p. 125° - 6°C.

The amount obtained was insufficient for analysis.

Although the product was not pure, it was evident that only one carboxyl group had been removed and that a monocarboxylic acid was formed. Fluoranthene-4-carboxylic acid has been prepared by Braun and Manz (Ann., 1931, 488, 111) and found to have a m.p. of 264° - 275°C. Easton (Ph.D. Thesis. Edin.Univ. Dec. 1947) found that it melted at 281° - 2°. Mixed m.p. with

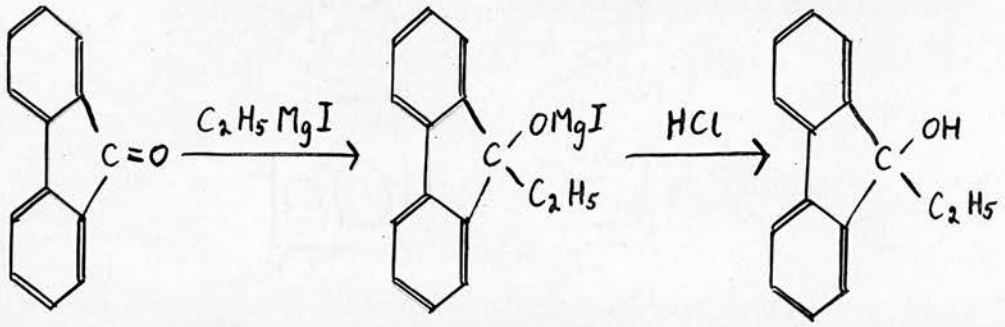
fluoranthene-4-carboxylic acid 225° - 275°C.

It was thus concluded that the acid obtained was not identical with fluoranthene-4-carboxylic acid and so must be fluoranthene-3-carboxylic acid. Furthermore, fluoranthene-4-carboxylic acid is readily decarboxylated under the conditions of the experiment and so could not have been isolated.



XXIII Synthesis of 2-methylfluoranthene.

1st Stage:- Preparation of 9-ethyl-9-hydroxyfluorene.



The method described by Ullmann and Wurstemberger (Ber., 1905, 38, 4105) was employed.

2·6 g. magnesium.

16·0 g. ethyl iodide.

200 c.c. anhydrous ether.

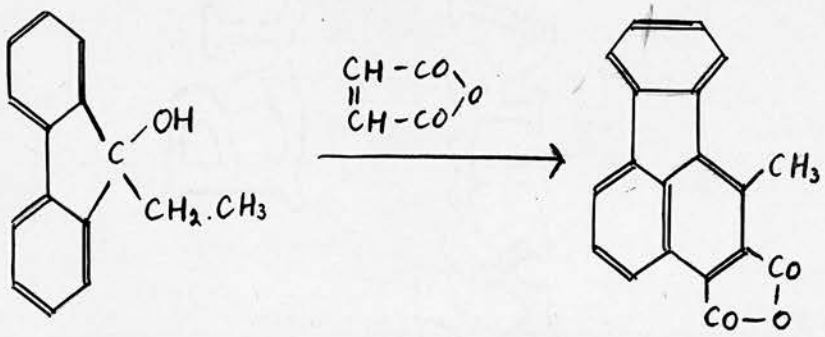
9·0 g. fluorenone dissolved in anhydrous ether.

The Grignard reagent was formed with vigorous stirring and the fluorenone then added. After refluxing for 20 minutes the complex was decomposed and isolated as in the preparation of 9-methyl-9-hydroxyfluorene. The solid was crystallised three times from light petroleum (b.p. 60° - 80°).

m.p. 96° - 98°C. lit. m.p. 101°C.

Yield 4·0 g. 38%.

2nd Stage:- <u>Preparation of 2-methylfluoranthene-3:4-dicarboxylic acid anhydride</u>.



0·5 g. 9-ethyl-9-hydroxyfluorene.

1·25 g. maleic anhydride.

10 c.c. acetic anhydride.

This solution was refluxed for 4½ hours. Acetic acid and water were added, whereupon a buff precipitate was obtained, which was insoluble in boiling sodium hydroxide, alcohol, glacial acetic acid and light petroleum. The solid was soluble in benzene, chlorobenzene, nitrobenzene and ethyl acetate.

Crystallised twice from benzene and light petroleum. An amorphous white solid was obtained.

m.p. 281° - 5°C.

Yield 0·42 g.

This appeared to be a polymer.

0·5 g. 9-ethyl-9-hydroxyfluorene.

1·5 g. maleic anhydride.

20 c.c. nitrobenzene.

The solution was refluxed for 2½ hours. The solution was cooled and allowed to stand overnight. Brown needles were obtained which were filtered and washed with alcohol.

m.p. 270° - 275°C. (Softened at 265°C).

On recrystallising from tetralin, long yellow needles, with a yellow fluorescence, separated.

m.p. 275° - 280°C. (with slight decomposition)

Yield 0·28 g. 41%.

This compound was insoluble in boiling alcohol and

light petroleum; sparingly soluble in boiling benzene and acetic acid; insoluble in boiling sodium hydroxide but soluble in boiling alcoholic potassium hydroxide. This solution, on acidification, gave a white gelatinous precipitate which readily reverted back to the anhydride.

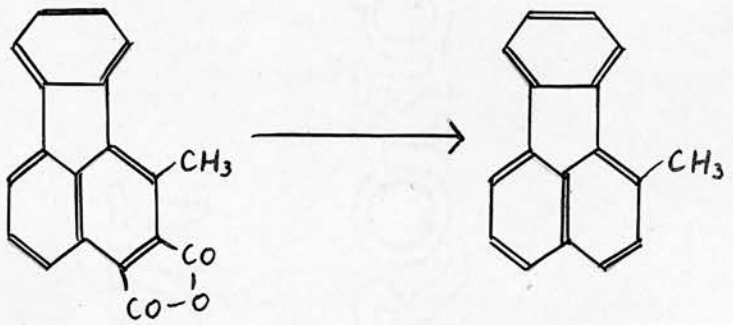
Analysis: fd. C = 78·65% H = 3·60%.

$C_{19}H_{10}O_3$ requires C = 79·69% H = 3·52%.

Thus the condensation was accompanied by dehydrogenation.

No ester could be prepared as the anhydride was insoluble in boiling alcohol.

3rd Stage:- Preparation of 2-methylfluoranthene.



0·2 g. 2-methylfluoranthene-3:4-dicarboxylic acid anhydride was mixed with 10 times its bulk of calcium hydroxide and heated in a pyrex tube as in the preparation of fluoranthene. The 2-methylfluoranthene sublimed along the tube. A little unchanged anhydride was removed by passing a benzene solution through a

short column of alumina. The hydrocarbon was recrystallised from light petroleum (b.p. 60° - 80°). Pale yellow needles were obtained.

m.p. 72° - 73°C.

Yield 0·10 g. 75%.

This compound showed a livid blue fluorescence in ultra violet light.

Analysis: fd. C = 94·40% H = 5·75%

$C_{17}H_{12}$ requires C = 94·38% H = 5·60%

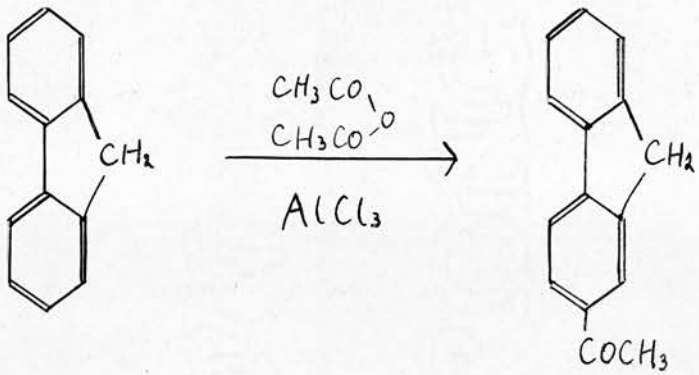
Picrate - orange needles. m.p. 207° - 208°C.

Analysis: fd. N = 9·35%

$C_{23}H_{15}O_7N_3$ requires N = 9·43%

XXIV Diels-Alder reaction on 2-ethyl-9-methyl-9-hydroxyfluorene.

1st Stage:- Preparation of 2-acetylfluorene.



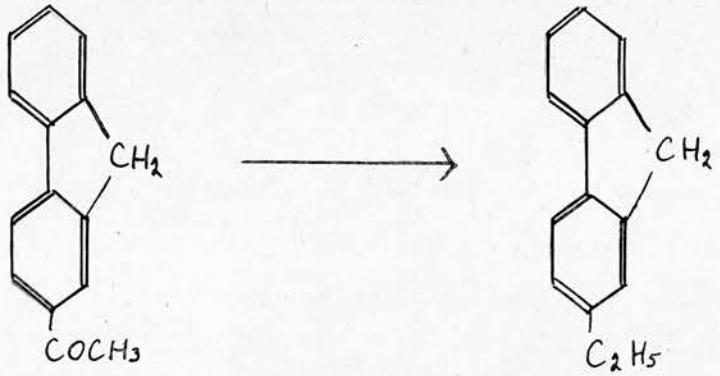
The conditions of Ray and Rieveschl (J.A.C.S., 1943, 65, 836) were followed.

Fluorene (80 g.) was acetylated with acetic anhydride (38 c.c.) using aluminium chloride (114 g.) in carbon disulphide (350 c.c.). The crude 2-acetylfluorene (105 g.) was recrystallised from alcohol.

m.p. 132°C. lit. m.p. 132°C.

Yield 64 g. 64%.

2nd Stage:- Preparation of 2-ethylfluorene.



60 g. zinc dust.

100 c.c. toluene.

35 c.c. water.

50 c.c. concentrated hydrochloric acid.

25 g. 2-acetylfluorene.

The zinc dust was amalgamated by shaking in the cold with 5 g. mercuric chloride in 75 c.c. water to which had been added 2½ c.c. concentrated hydrochloric acid. After a few minutes, the supernatent liquid was

poured off and the toluene, water, hydrochloric acid and 2-acetylfluorene were added. The mixture was refluxed briskly for 24 hours with the addition of 25 c.c. concentrated hydrochloric acid after every 6 hours. The solution was cooled, extracted with ether, dried with calcium chloride and the ether evaporated off. A brown oily solid was obtained which did not crystallise well from any solvent. This material was distilled under reduced pressure and the fraction b.p. 170° - 175°C/15 m.m. was collected. The distillate solidified and was recrystallised from light petroleum (b.p. 40° - 60°). White plates were obtained.

m.p. 81° - 82°C.

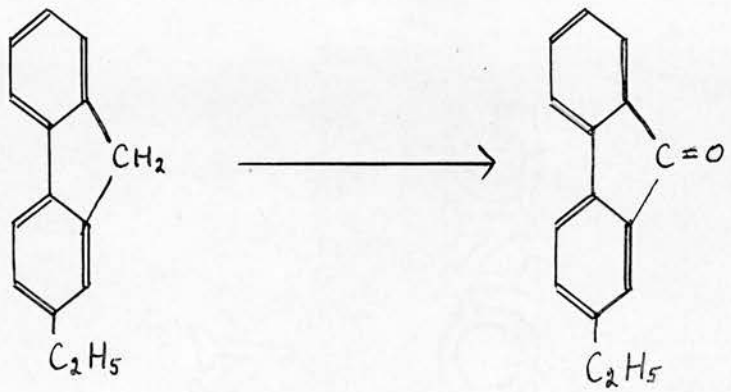
Yield 10·4 g. 41%.

2-Ethylfluorene sublimes readily and possesses a bright blue fluorescence in solution.

Analysis: fd. C = 92·80% H = 6·94%.

$C_{15}H_{14}$ requires C = 92·74% H = 7·26%.

3rd Stage:- Preparation of 2-ethylfluorenone.



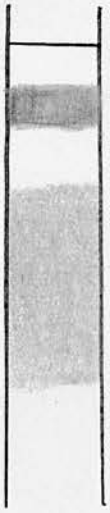
To the boiling solution of 2-ethylfluorene (12·0 g.) in glacial acetic acid (25 c.c.) was added slowly a solution of sodium dichromate (12·5 g.) in glacial acetic acid (25 c.c.). The solution was refluxed for 2 hours, cooled, extracted with ether, washed with water, dried with calcium chloride and evaporated to dryness. On crystallising three times from light petroleum (b.p. 60° - 80°), yellow prisms were obtained.

m.p. 115° - 119°C.

Yield 5·5 g. 43%.

This was found to be essentially 2-ethylfluorenone but there was also a small quantity of 2-acetylfluorenone.

A small portion of this product was purified by chromatographic adsorption. A benzene solution was passed through a column of alumina, and the chromatogram was developed with a 1:3 mixture of benzene: light petroleum (b.p. 60° - 80°). Two yellow bands were obtained, both yielding yellow solids on evaporating to dryness. The more easily eluted band amounted to 95% of that recovered from the column.



This first band was recrystallised from light petroleum (60° - 80°). Yellow plates of 2-ethylfluorenone.

m.p. 127° - 128°C.

Analysis: fd. C = 85·86% H = 5·88%.

$C_{15}H_{12}O$ requires C = 86·51% H = 5·81%

2:4-dinitrophenylhydrazone —— red needles.

m.p. 267° - 8°C.

Analysis: fd. N = 13·8%

$C_{21}H_{16}N_4O_4$ requires N = 14·4%.

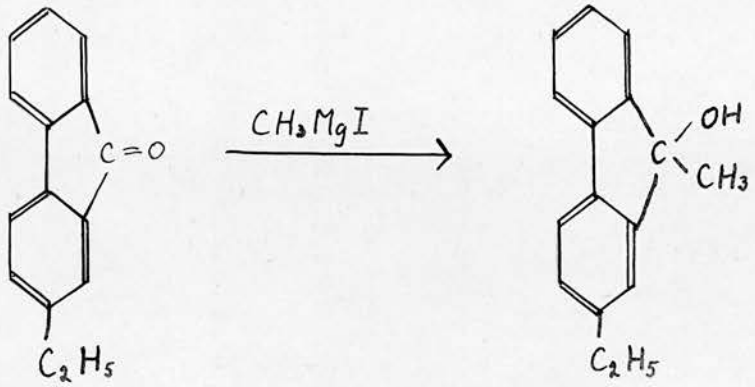
The second band (amounting to 5% of total) was recrystallised from light petroleum (b.p. 60° - 80°). Yellow prisms of 2-acetylfluorenone.

m.p. 156° - 7°C. lit. m.p. 154° - 5°C.

Analysis: fd. C = 80·42% H = 4·95%

Calc. for $C_{15}H_{10}O_2$ C = 81·06% H = 4·54%

4th Stage:- Preparation of 2-ethyl-9-methyl-9-hydroxyfluorene.



The procedure adopted was similar to the procedure adopted for the preparation of 9-methyl-9-hydroxyfluorene.

6 g. 2-ethylfluorenone in 300 c.c. anhydrous ether.

2 g. magnesium powder.

16 g. methyl iodide.

50 c.c. anhydrous ether.

The methyl iodide was slowly added to a suspension of the magnesium in the ether with brisk stirring. The solution of 2-ethylfluorenone was then slowly added while the stirring was continued. After the addition was complete, the solution was refluxed for ½ hour, cooled and decomposed on ice. The solution was acidified, washed with sodium bisulphite, water, dried and the ether allowed to evaporate off at room temperature. The residue was crystallised from benzene.

Colourless needles.

m.p. 124° - 125°C.

Yield 2·8 g. 43%.

Analysis: fd. C = 85·66% H = 6·84%

$C_{16}H_{16}O$ requires C = 85·67% H = 7·19%

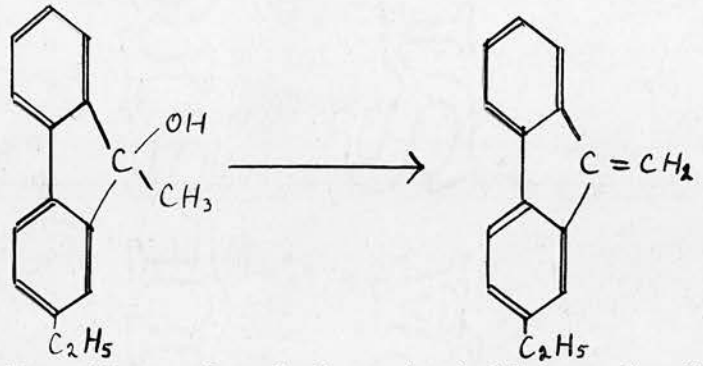
It was found, however, that if the ether was taken off on the steam bath then dehydration occured to give

2-ethyl-9-methylenefluorene. Prolonged heating on the steam bath produced a brittle resin. 2-ethyl-9-methylenefluorene was recrystallised from benzene.

Colourless plates m.p. 156° - 7°C.

Analysis: fd. C = 93·03% H = 6·75%. M.W. = 220.

$C_{16}H_{14}$ requires C = 93·16% H = 6·84%. M.W. = 206.



5th Stage: Reaction of maleic anhydride on 2-ethyl-9-methyl-9-hydroxyfluorene.

0·25 g. 2-ethyl-9-methyl-9-hydroxyfluorene.

1·00 g. maleic anhydride.

5 c.c. acetic anhydride.

This solution was refluxed for 2 hours. The solution gradually darkened to give a deep red colour. The solution was cooled and allowed to stand overnight but no condensation product separated out. On adding glacial acetic acid, a white amorphous precipitate was obtained. This substance was found to be insoluble in boiling sodium hydroxide, glacial acetic acid, benzene, alcohol and light petroleum. It was soluble in boiling acetic

anhydride and dichlorobenzene but did not crystallise from these solvents. The material could be recovered by precipitation from the solvents by acetic acid and benzene respectively.

m.p. 295° - 305°C (with decomposition)

This substance had all the appearances of a polymer.

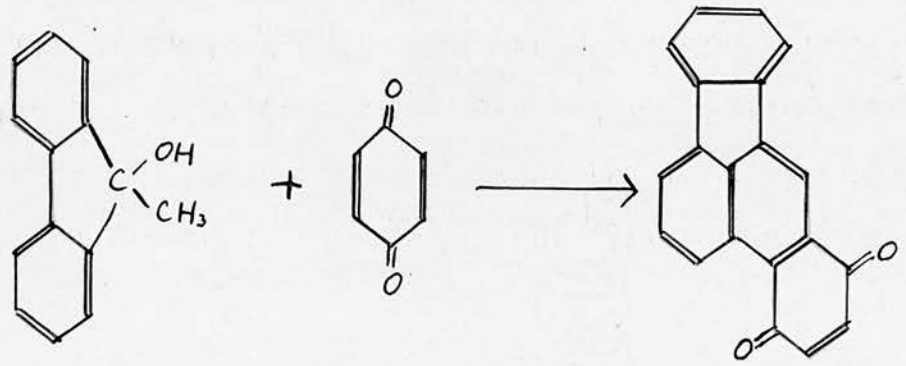
0·25 g. 2-ethyl-9-methyl-9-hydroxyfluorene.

1·00 g. maleic anhydride.

5 c.c. nitrobenzene.

This solution was refluxed for 1½ hours turning dark brown. On cooling, no precipitate was obtained although left overnight. A black oily solid separated out on adding benzene and light petroleum. This solid was insoluble in boiling sodium hydroxide, alcohol, benzene and acetic acid; sparingly soluble in boiling chlorobenzene and dichlorobenzene. It was soluble in boiling tetralin but did not crystallise on cooling. A black oily solid was obtained from this solution on addition of light petroleum. This material was unable to be purified but it had ~~not~~ the properties of a polymerised product.

XXV. Preparation of 3,4-benzfluoranthene-1':4'-quinone.



2·5 g. 9-methyl-9-hydroxyfluorene.

10 g. p-benzoquinone.

50 c.c. acetic anhydride.

The solution was refluxed for 2 hours when a red solid began to separate from the hot dark red solution. On cooling, orange-red needles were obtained which were recrystallised from glacial acetic acid.

m.p. 245° - 6°C.

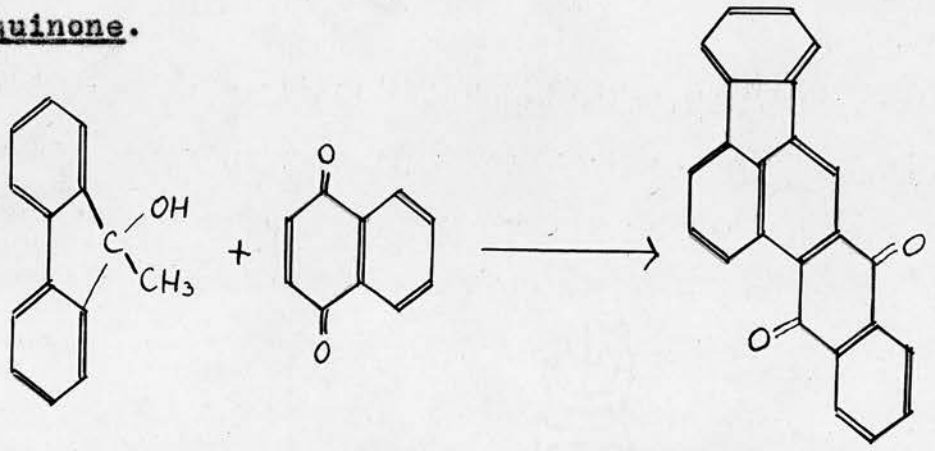
Yield 0·90 g. 25%.

This quinone gave a purple colouration in cold concentrated sulphuric acid and a wine red vat with sodium hydrosulphite ($Na_2S_2O_4$).

Analysis: fd. C = 84·10% H = 3·65%.

$C_{20}H_{10}O_2$ requires C = 85·10% H = 3·57%

XXVI. Preparation of 3,4:2',3'-naphthfluoranthene-1':4'-quinone.



2·5 g. 9-methyl-9-hydroxyfluorene.

10 g. 1:4-naphthoquinone.

50 c.c. acetic anhydride.

This solution was refluxed for 2 hours when a red precipitate began to separate from the hot dark red solution. On cooling, orange-red needles were obtained which were recrystallised from nitrobenzene and light petroleum (b.p. 100° - 120°C).

m.p. 249° - 251°C.

Yield 0·50 g. 12%.

This quinone gave a blue-green colouration in cold concentrated sulphuric acid and a blue violet vat with sodium hydrosulphite ($Na_2S_2O_4$).

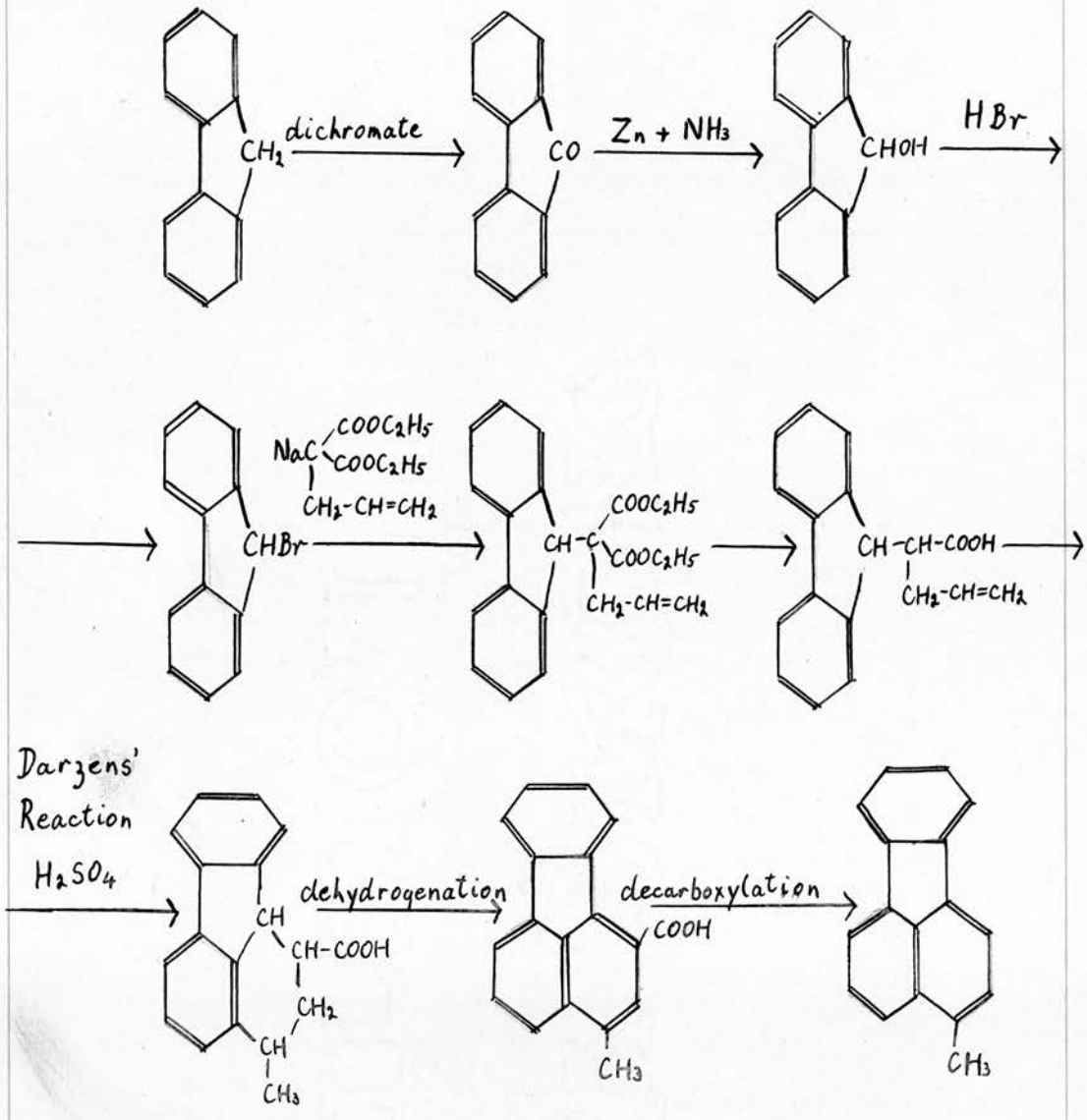
Analysis: fd. C = 86·35% H = 3·70%.

$C_{24}H_{12}O_2$ requires C = 86·73% H = 3·63%.

DISCUSSION

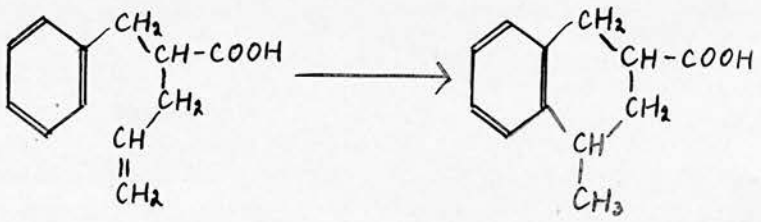
(A) Darzens' Synthesis.

The first synthesis attempted involved cyclisation by means of the Darzens' reaction (42) as outlined in the following scheme:-



The Darzens' reaction involves the cyclisation of aromatic compounds containing a side-chain with a carboxyl group and a double bond by sulphuric acid. Darzens found that the γ-lactones of these acids could also be cyclised under certain conditions but the δ-lactones could not.

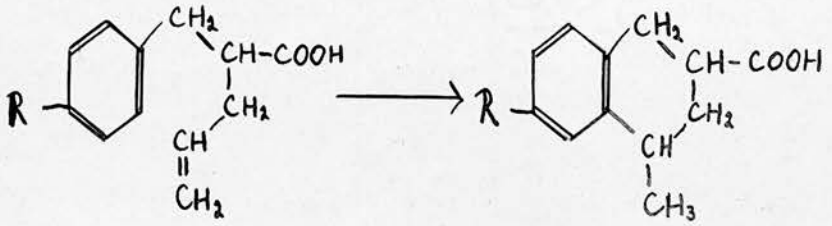
A good example of the reaction is furnished by allylbenzylacetic acid which Darzens (21) cyclised with 78% sulphuric acid at 0° C for 5 hours



Allylbenzylacetic acid was prepared by benzylation and allylation of malonic ester followed by hydrolysis and decarboxylation. The resulting naphthalene derivative was dehydrogenated by heating with sulphur.

The γ-lactone of this acid was cyclised with 64·5% sulphuric acid at 120° - 125° C for 8 days (22).

Various compounds have been prepared and cyclised in a similar manner.

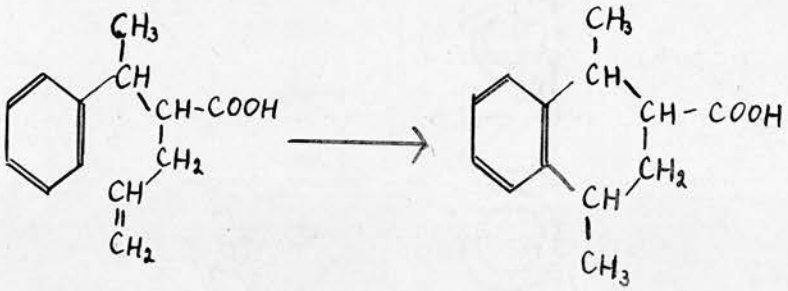


R = CH_3- Cyclisation with 78% sulphuric acid in the cold (24).

R = $(CH_3)_2CH$- Cyclisation with 84% sulphuric acid in the cold for 5 days (26).
(γ & δ lactones were formed but only the γ-lactone could be cyclised).

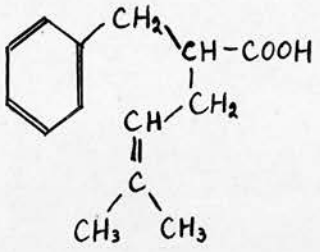
R = $(CH_3)_3C$- Cyclisation with 84% sulphuric acid in cold for 3 days (28).

R = CH_3O- Cyclisation with 80% sulphuric acid in cold for 48 hours (29).
(γ-lactone cyclised with 45% sulphuric acid but δ-lactone did not cyclise).

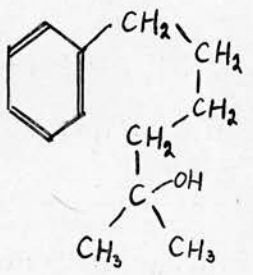


Cyclisation with 65% sulphuric acid at 120° - 125°C for 8 days (23).

Darzens and Levy (25) found that the only acid of this type which failed to cyclise was α-benzyl-δ- methyl-Δ^{γ}-hexenecarboxylic acid.



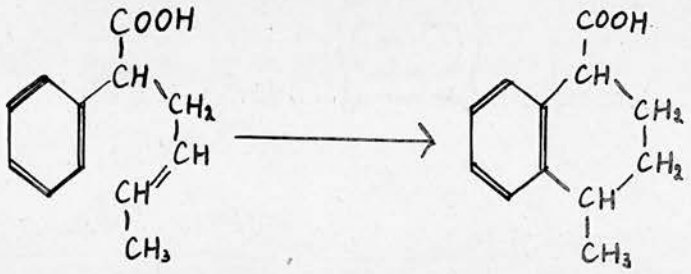
The carboxyl group appeared to inhibit cyclisation since Bogert, Davidson and Roblin (6) found that α:α-dimethyl-ε-phenylpentanol underwent cyclodehydration.



Darzens and Levy (30,31) applied this reaction to the synthesis of phenanthrene derivatives from which they prepared 1-methylphenanthrene and 1:5-dimethyl-phenanthrene.

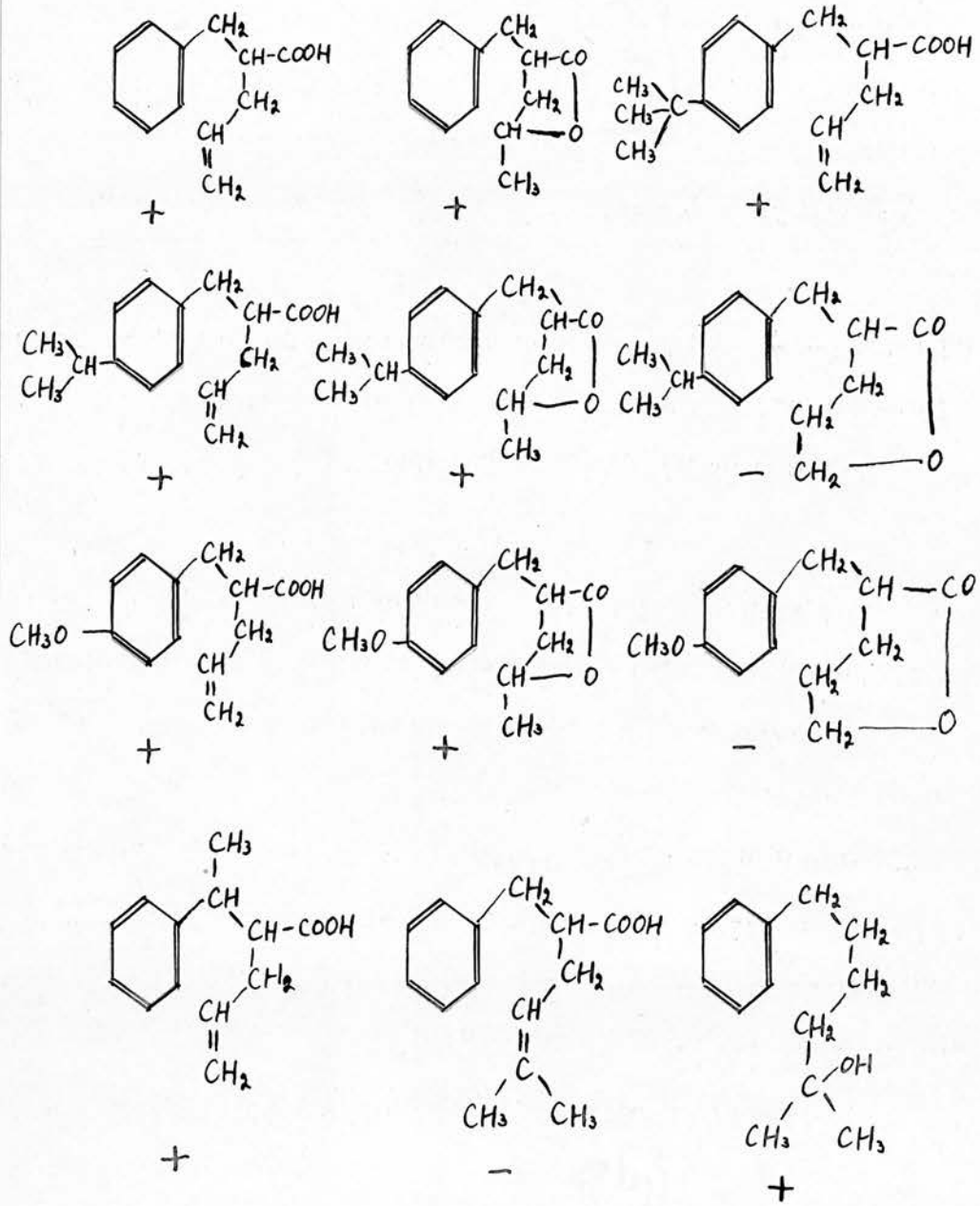
This reaction has been applied mainly to compounds

where the acid group is in the β-position from the benzene ring, but Darzens and Levy (27) observed the cyclisation of the following α-acid.



SUMMARY.

Where the cyclisation was successful, the compound is marked with + ; where unsuccessful it is marked with − .



I and II. Attempted ring closure of 9-fluorenylallylacetic acid.

9-Bromofluorene was prepared by the reduction of fluorenone to 9-fluorenol followed by conversion with hydrogen bromide. Staudinger (48) carried out this conversion but did not give full experimental details. It was found that a 66% yield was obtained by saturating a glacial acetic acid solution of 9-fluorenol with dry hydrogen bromide and then warming for a short time. Recently Hurd and Mold (39) found that saturation in the cold gave a 40% yield of 9-bromofluorene while in the hot, condensation products were obtained. They obtained, however, a 66% yield by shaking in the cold with 41% hydrogen bromide solution for 36 hours.

9-Bromofluorene was also prepared by the bromination of fluorene with N-bromosuccinimide (53). It was found, however, that very pure N-bromosuccinimide was essential for bromination to proceed smoothly (54).

All the malonic ester condensations were carried out in a manner similar to that described by Adams and Ramm (1). Diethyl 9-fluorenylallylmalonate was prepared either by direct condensation of 9-bromofluorene with diethyl allylmalonate or by condensing 9-bromofluorene

first with diethyl malonate, then with allyl bromide. Both these methods yielded oils which did not solidify in an ice-salt mixture and which could not be distilled under reduced pressure without decomposition. Both oils, however, when hydrolysed and decarboxylated gave 9-fluorenylallylacetic acid.

The cyclisation was tried under various conditions without success. With sulphuric acid, it was found that in some cases no reaction occurred and the starting material was obtained unchanged. When more drastic conditions were tried, it was found that sulphonation and charring occurred. Phosphoric acid also has been used for similar compounds (5,6) but with 9-fluorenylallylacetic acid, it proved to be unsuccessful. A mixture of sulphuric and phosphoric acids has been used (38). When the reaction was conducted below $0^{\circ}C$, no cyclisation occurred. When the temperature was raised to 45° - $50^{\circ}C$, again no cyclisation occurred but the reaction was accompanied by some sulphonation.

The failure of 9-fluorenylallylacetic acid to undergo ring-closure may be due to its insolubility in sulphuric acid in contrast to the benzene derivatives used by Darzens.

Another reason may be the comparative inert nature

cf., Lowens, Tucker et al. J., 1945, 7

of position 1- in the fluorene nucleus (e.g. substitution occurs mainly at the 2- and 7- positions and to a lesser extent at the 5- but not at the 1-). When ring-closure is effected at position 1- (16) a stronger reagent (aluminium chloride) is required.

III. Preparation of 1:2:3:4-tetrahydro-4-methyl-2-naphthoic acid.

When 9-fluorenylallylacetic acid failed to cyclise, it was decided to investigate the Darzens' reaction by starting with a simple compound and gradually building up the size and complexity of the molecule. The cyclisation of allylbenzylacetic acid was a repetition of the work of Darzens (21).

Allylbenzylacetic acid was prepared by malonic ester condensation followed by hydrolysis and decarboxylation. The cyclisation proceeded smoothly under the conditions given by Darzens, and it was noted that allylbenzylacetic acid was completely miscible with the sulphuric acid.

IV. Preparation of 1:5-dimethylnaphthalene.

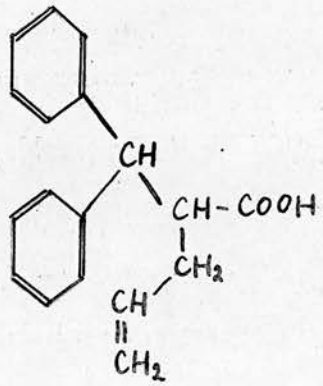
The cyclisation was repeated with a methyl group added to the benzene ring.

o-Xylene was brominated forming o-methylbenzyl

bromide which was condensed with allylmalonic ester. o-Xylylallylacetic acid was formed by hydrolysis of the product and decarboxylation. The cyclisation proceeded easily with 80% sulphuric acid in the cold for 5 hours. The resulting 1:2:3:4-tetrahydro-4:8-dimethyl-2-naphthoic acid was dehydrogenated with chloranil to give 4:8-dimethyl-2-naphthoic acid which was decarboxylated by heating to 215° - 220°C with quinoline and copper bronze. The 1:5-dimethylnaphthalene thus obtained was identified by m.p. and by m.p. of picrate.

An attempt to decarboxylate 1:2:3:4-tetrahydro-4:8-dimethyl-2-naphthoic acid with quinoline and copper bronze failed. Probably this method of decarboxylation can be applied only to compounds where the carboxyl group is directly attached to an aromatic ring.

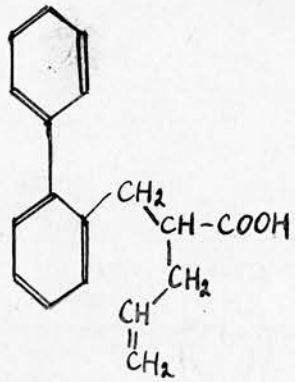
V and VI. Attempted cyclisation of 1-(diphenylmethyl)-Δ^3-pentenic acid.



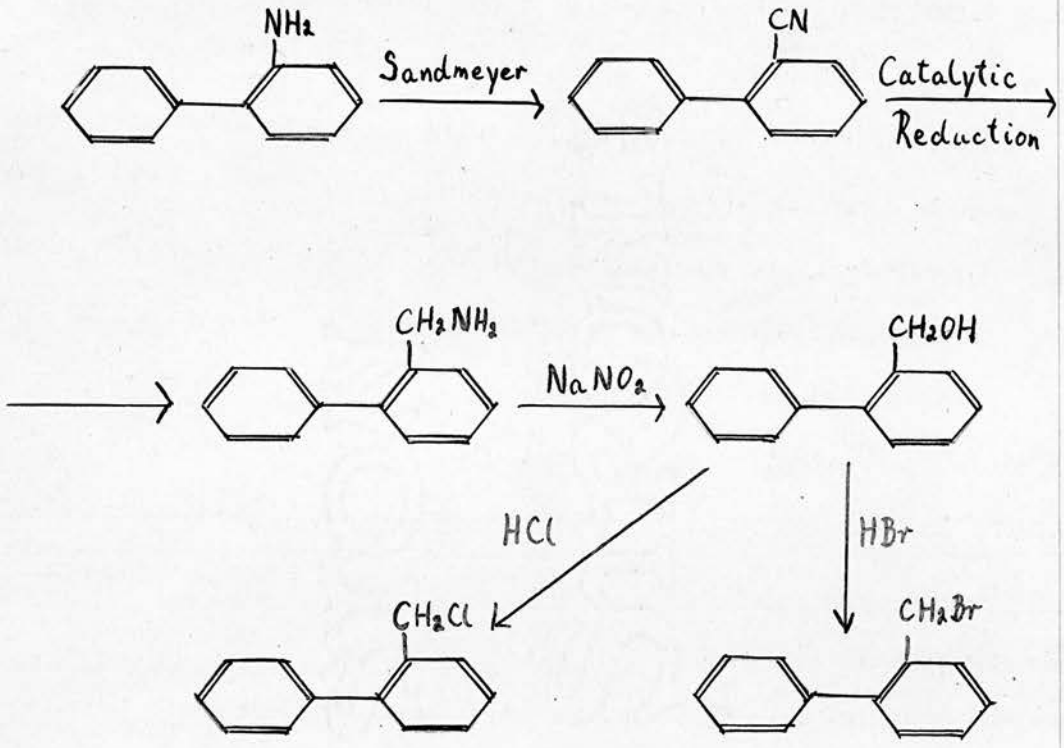
1-(diphenylmethyl)-Δ^3-pentenic acid was prepared from diphenylmethyl bromide in order to study the cyclisation of a diphenylmethane derivative. All attempts to cyclise this compound with sulphuric or phosphoric acids failed, probably due to its insolubility in sulphuric acid.

VII Preparation of 2-methyldiphenyl.

It was intended to investigate the cyclisation of o-phenylbenzylallylacetic acid to note the effect of adding a benzene ring to the aromatic nucleus.



To obtain this compound, the preparation of o-phenylbenzyl bromide or chloride was required. Both of these compounds have been prepared by von Braun and Manz (17). Their method (summarised below) required many steps so that the amount of starting material required would be prohibitive if an appreciable quantity of the halide was to be obtained.



It was hoped that o-phenylbenzyl chloride would be obtained in good yield by the direct chlorination of 2-methyldiphenyl.

2-Methyldiphenyl was prepared from o-toluidine. o-Toluidine was diazotised and converted into o-bromotoluene through a Sandmeyer reaction (4). o-Bromotoluene was then converted into 1-o-tolylcyclohexanol by means of a Grignard reaction with cyclohexanone (44,47). This alcohol was dehydrated by shaking with concentrated

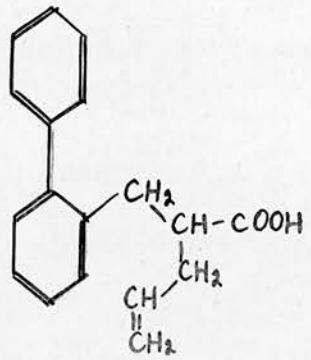
formic acid. The final dehydrogenation was carried out in good yield by means of chloranil and the 2-methyldiphenyl distilled under reduced pressure.

A one stage preparation of 2-methyldiphenyl by Oddo and Curatolo (43) was tried but the yield was negligible.

VIII Attempted chlorination of 2-methyldiphenyl.

The chlorination of 2-methyldiphenyl was tried with sulphuryl chloride in presence of a peroxide as chlorinating reagent. The resulting oil was distilled under reduced pressure but consisted mainly of unchanged 2-methyldiphenyl. A small amount of higher boiling fraction was obtained which was analysed. This oil contained some chlorine so it seemed as if partial chlorination had taken place. This indicated that the chlorination did not occur readily, a possible explanation being the steric effect of the benzene ring in the o-position.

IX,X,XI and XII Attempted preparation of allyl(o-phenylbenzyl)acetic acid.



It was found that N-bromosuccinimide could be used successfully to brominate 2-methyldiphenyl in the side chain provided care was taken to purify the brominating reagent before use.

The malonic ester condensation was carried out and the diethyl ester isolated. Although the hydrolysis was performed in two ways, oils were obtained which could not be purified. Decarboxylation was carried out but an intractable oil was obtained.

As allyl(o-phenylbenzyl)acetic acid could not be obtained in a pure state, attempts were made to cyclise the diethyl ester. This, however, met with failure.

XIII Preparation of ethyl o-phenylbenzoate.

As the best procedure for the use of N-bromosuccinimide was not discovered till late in the research, other routes to the preparation of o-phenylbenzyl bromide or chloride were investigated.

It was hoped that these compounds might be obtained from o-phenylbenzyl alcohol prepared through the reduction of ethyl o-phenylbenzoate.

Fluorenone was fused with potassium hydroxide to give diphenyl-2-carboxylic acid (37) which was converted into the ethyl ester.

XIV Attempted reduction of ethyl o-phenylbenzoate.

A modification of the Bouveault and Blanc method developed by Prins (45) was tried. The ester was dissolved in ether and a saturated solution of sodium acetate added to form a lower layer. The reduction was carried out by the slow addition of sodium, the solution being kept neutral or slightly acid by the addition of 30% acetic acid. By this means the reduction was carried out slowly over a number of days.

The resulting oil distilled at 160° - 170°C/13 mm. but this was almost all unchanged ester. A very small amount of oil was obtained which was converted into a p-nitrobenzoate which appeared to be impure p-nitrobenzoate of o-phenylbenzyl alcohol.

The Bouveault and Blanc reduction (with its various modifications) has been applied only to aliphatic esters

and to aromatic compounds with the carboxyl group attached to a side chain. No mention has been found in the literature to the satisfactory reduction of an ester where the carboxyl group has been directly attached to an aromatic ring.

XV and XVI Ullmann reaction on o-bromobenzonitrile and iodobenzene.

In a further attempt to obtain o-phenylbenzyl bromide or chloride, the preparation of 2-cyanodiphenyl was tried. It was hoped that an Ullmann reaction between o-bromobenzonitrile and iodobenzene would give 2-cyanodiphenyl, which could be easily converted into the required halogen compound.

Dehydration of o-bromobenzamide with phosphorus oxychloride gave o-bromobenzonitrile. The Ullmann reaction resulted in an oily solid which could not be purified.

XVII and XVIII Attempted preparation of 2-methyl-2'-chloromethyldiphenyl.

It was next decided to attempt the preparation of 2-methyl-2'-chloromethyldiphenyl from 2:2'-dimethyldiphenyl

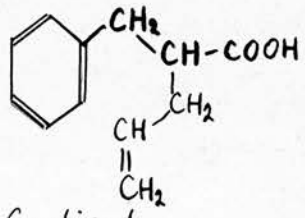
which could be obtained more easily than 2-methyldiphenyl. o-Iodotoluene underwent an Ullmann reaction to give 2:2'-dimethyldiphenyl. Ullmann (49) accomplished this by heating the reactants in a sealed tube at 230°C for 3 hours. It was found, however, that only a low yield could be obtained under these conditions but if the temperature was raised to 280°C and the time doubled, the reaction proceeded in 62% yield. This is contrary to the findings of Kenner and Turner (41) who obtained the best yields at 230°C.

An attempt was made to chlorinate 2:2'-dimethyldiphenyl using sulphuryl chloride in presence of a peroxide. As in the case of the chlorination of 2-methyldiphenyl, only a little chlorination took place, the bulk of the reaction product being unchanged 2:2'-dimethyldiphenyl.

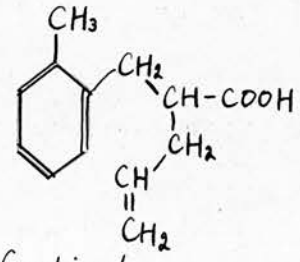
The probable reason for the difficulty in the chlorination was the steric hindrance of the neighbouring benzene ring.

Summary of Work on the Darzens Reaction.

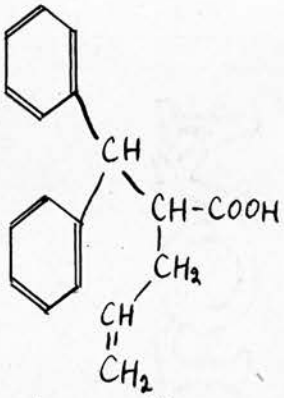
The following compounds have been investigated.



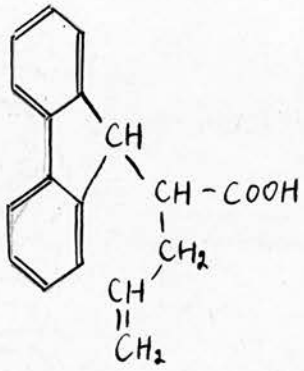
Cyclised



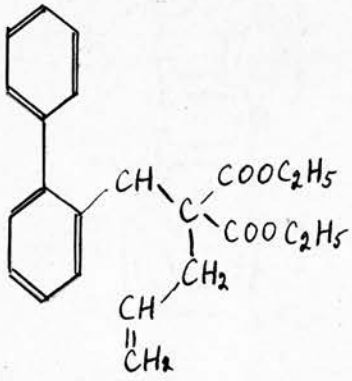
Cyclised



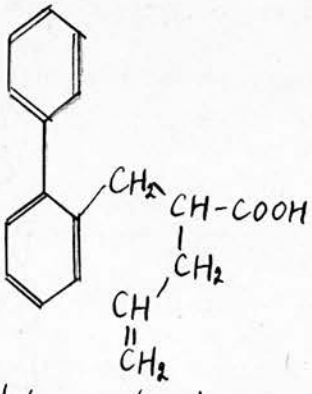
Did not cyclise



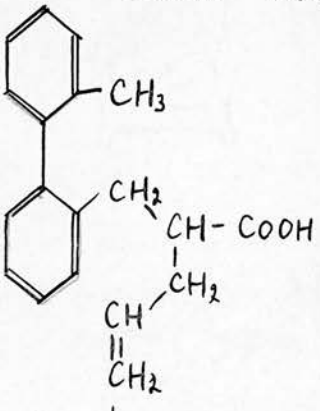
Did not cyclise.



Did not cyclise



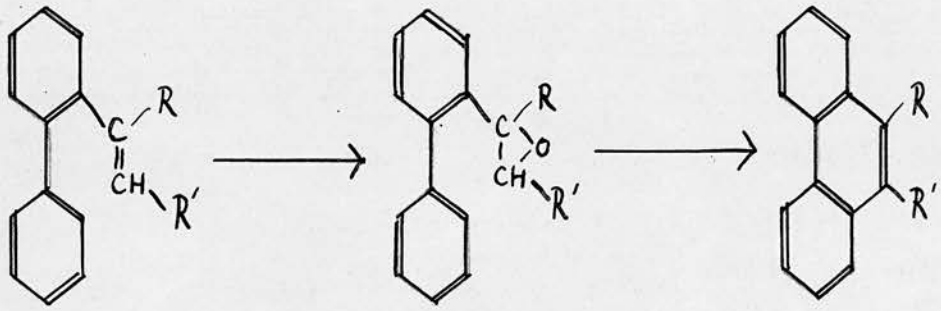
Could not be prepared



Could not be prepared.

(B) Cyclodehydration of Epoxide.

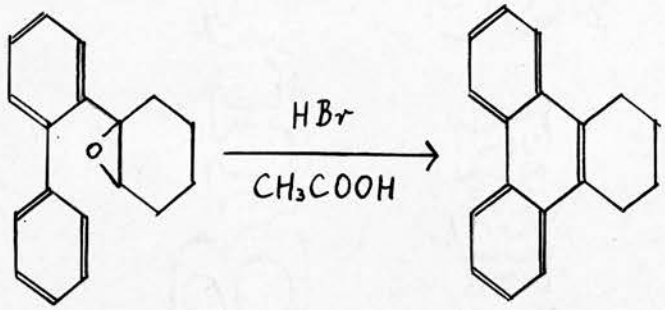
Phenanthrene and a number of phenanthrene derivatives have been prepared by the cyclisation of epoxides. Ethylene derivatives of diphenyl are oxidised with perbenzoic acid or monoperphthalic acid to form epoxides which are cyclised by refluxing in a mixture of hydrobromic and acetic acids. The general equation is:-



Where R and R' are H, CH_3, C_2H_5, C_6H_5 etc.

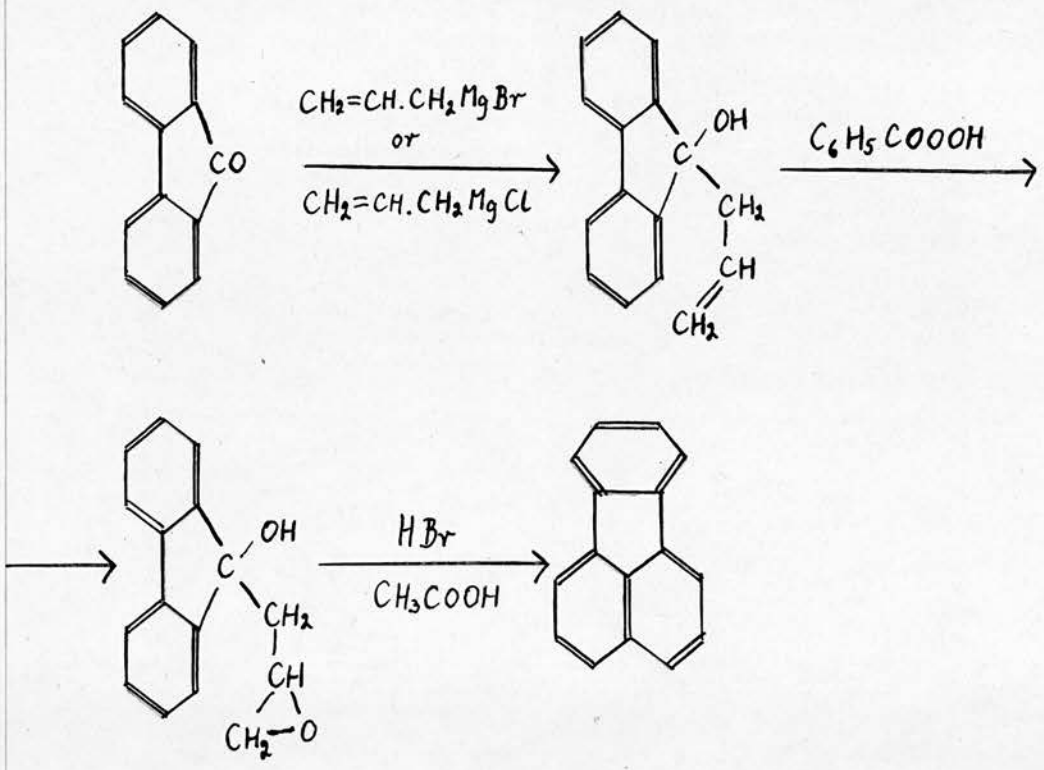
The conditions for these experiments were given by Bradsher and Wert (14) and Bradsher and Amore (9,10,11).

This reaction had been first applied to oxides of various cycloolefines by Bradsher (8) and Bradsher and Rapopart (12, 13). The simplest reaction of this series is represented by the equation:-



A summary of these reactions is given by Bradsher (7).

It was decided to attempt the synthesis of fluoranthene by a similar procedure. The proposed series of reactions was:-



XIX Preparation of 9-allyl-9-hydroxyfluorene.

Backer and Strating (2) used allyl magnesium bromide to prepare 9-allyl-9-hydroxyfluorene. Allyl magnesium bromide, however, reacts very readily with allyl bromide to form diallyl.

$$CH_2=CH.CH_2MgBr + CH_2=CH.CH_2Br \rightarrow CH_2=CH.CH_2.CH_2.CH=CH_2 + MgBr_2.$$

Gilman and McGlumphy (35) have given conditions by which allyl magnesium bromide could be prepared in good yield with freshly powdered magnesium. Unfortunately, the only magnesium available was in the form of coarse turnings which were suitable for most Grignard reactions but useless for the preparation of allyl magnesium bromide. The magnesium did not react rapidly enough with the allyl bromide to prevent the reaction of allyl magnesium bromide with allyl bromide. In no case could 9-allyl-9-hydroxyfluorene be isolated. Gilman and McGlumphy coupled allyl magnesium bromide with benzophenone. An attempt to repeat their work also failed.

Karasch and Fuch (40) have described the successful preparation and use of allyl magnesium chloride. They applied it to a variety of condensations and have recommended its use in preference to allyl magnesium bromide. Allyl magnesium chloride was prepared according to their conditions and coupled with fluorenone to give 9-allyl-9-hydroxyfluorene.

XX Preparation of 9-hydroxyfluorene-9-allylepoxide.

Perbenzoic acid was prepared from benzoyl peroxide by the method of von Braun (15). The perbenzoic acid was not isolated in a solid state but was kept in moist chloroform solution in the dark in a refrigerator. Owing to the slow decomposition of perbenzoic acid even under these conditions, the concentration of the acid in the solution was determined by iodometric titration just before use.

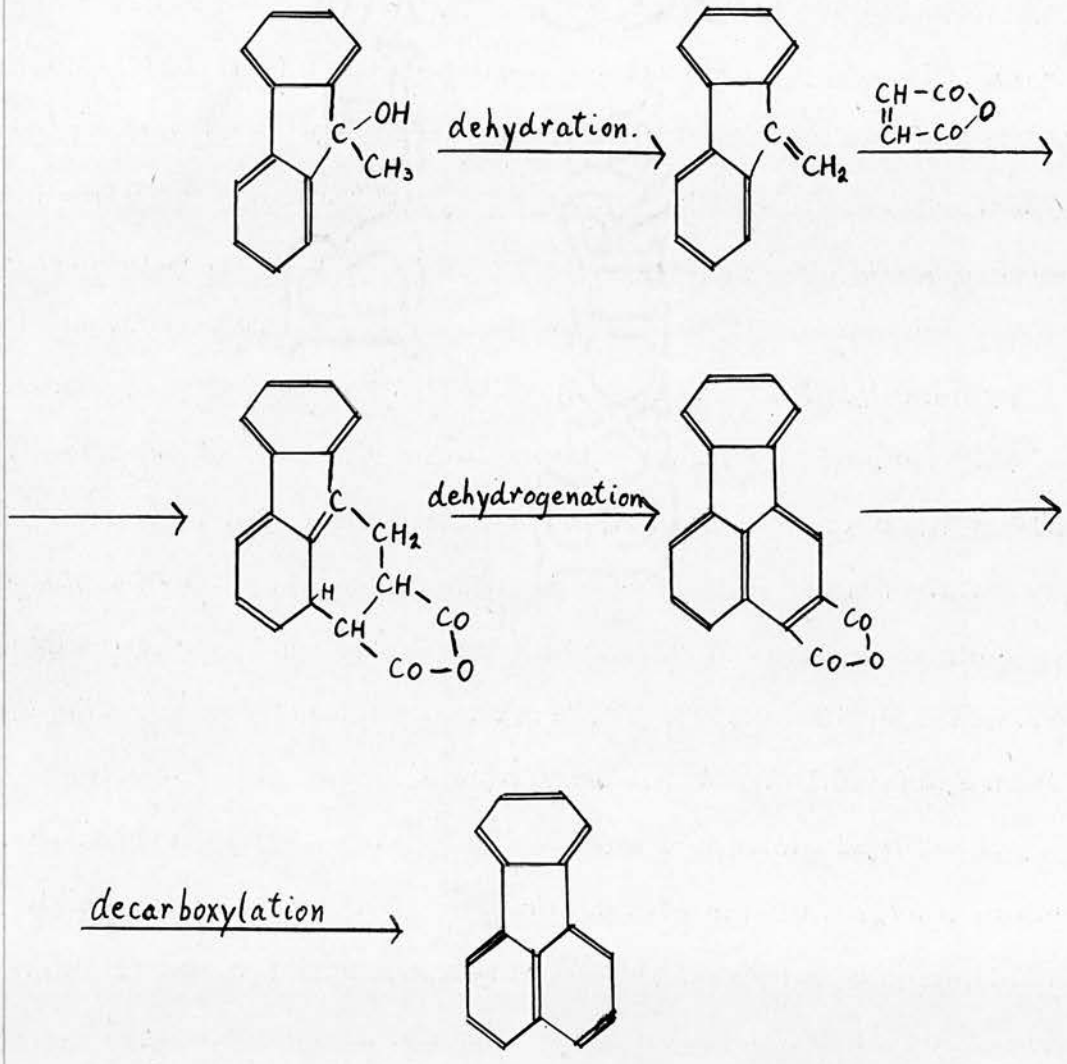
A slight excess of perbenzoic acid was used for the oxidation. At intervals samples were withdrawn and their concentration of perbenzoic acid determined by iodometric titration. In this way the length of time required, till no further reaction, was found.

XXI Attempted cyclisation of 9-hydroxyfluorene-9-allyle-poxide.

The cyclisation was attempted with a mixture of hydrobromic and acetic acids as dehydrating agent. It was found that as soon as dehydration started, the product polymerised to give a resinous substance which could not be purified or identified. No fluoranthene could be detected.

(C) Diels-Alder Syntheses.

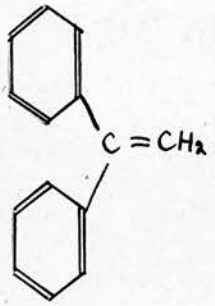
The Diels-Alder reaction has been used extensively for the preparation of organic compounds. It was thought that a synthesis of fluoranthene might be accomplished by the following stages.



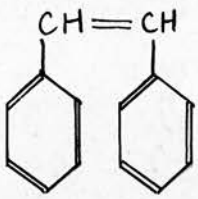
The course of the Diels-Alder reaction would be influenced by the following factors.

(a) The first is the stability of the intermediate compound, 9-methylenefluorene. It has been found by Wieland, Reindel and Ferrer (52) and Ferrer (33) that 9-methylenefluorene can be isolated but is very unstable and polymerises in daylight in a few minutes and in the dark in a few hours. It was felt that this difficulty might be surmounted by employing 9-methyl-9-hydroxyfluorene as the diene and carrying out the dehydration and condensation simultaneously.

(b) The second factor is the reactivity of an aromatic bond as part of a diene system. It was first discovered by Wagner-Jauregg (50,51) that an aromatic bond can participate in the Diels-Alder reaction. He found that α:α-diphenylethylene I underwent a Diels-Alder condensation with maleic anhydride to form a bis-adduct. Heteropolymerisation, however, occurred with a number of other compounds, namely stilbene II, isostilbene III, 9-benzalfluorene IV and 9-anisalfluorene V. α-Bromostilbene VI, tetraphenylethylene VII and α:β-dibenzylethylene VIII did not react at all with maleic anhydride.

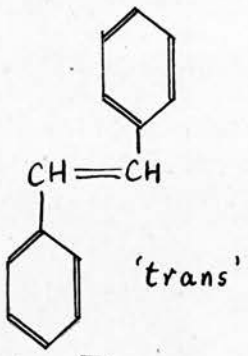


I



'cis'

II



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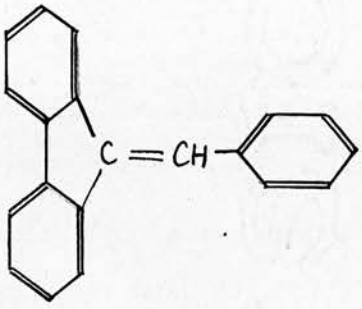

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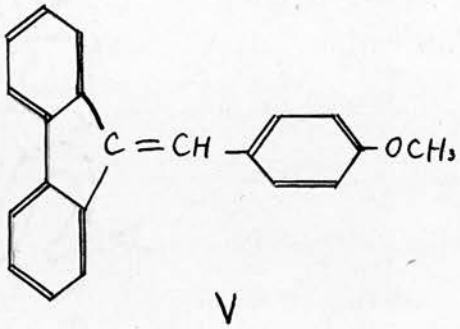

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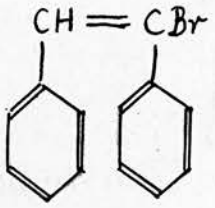


VI

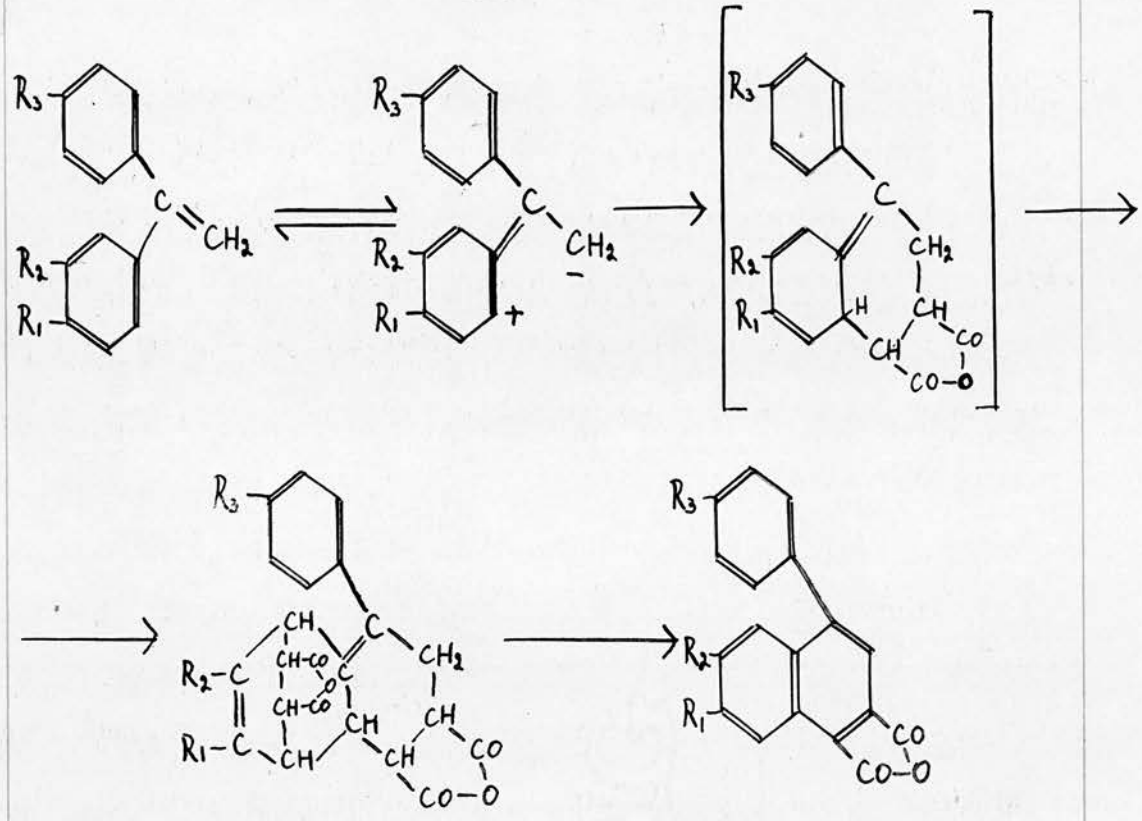
$(C_6H_5)_2C = C(C_6H_5)_2$

VII

$C_6H_5.CH_2.CH = CH.CH_2.C_6H_5$

VIII

Following the work of Wagner-Jauregg, many aromatic-aliphatic dienes have been found to undergo Diels-Alder condensations with dieneophils. In particular, Bergmann, Szmuskowiez and Pawez (3) made a study of substituted $\alpha:\alpha$-diphenylethylenes and found that bis-adducts were formed. viz.



Where R_1, R_2, R_3 were H, OCH_3, CH_3 or C_6H_5.

It seemed likely that 9-methylenefluorene would undergo condensation since the structures were similar.

XXII Synthesis of fluoranthene.

Condensation of 9-methyl-9-hydroxyfluorene with excess maleic anhydride in acetic anhydride gave an adduct which was found to be fluoranthene-3:4-dicarboxylic acid anhydride instead of the expected 1:2:3:4-tetrahydro-fluoranthene-3:4-dicarboxylic acid anhydride. The yield of the adduct was low and a polymerised product was also

isolated. Thus there were two competing reactions viz. condensation and polymerisation. It appeared as if disproportionation occurred so that the adduct was dehydrogenated to give a completely aromatic compound. The dimethyl ester of this anhydride was prepared but the free dicarboxylic acid seemed to be too unstable to be isolated and to revert back to the anhydride readily.

Heating with calcium hydroxide decarboxylated the anhydride to give fluoranthene which was identified by m.p., mixed m.p., m.p. of picrate, mixed m.p. of picrate and the colour reaction with concentrated sulphuric acid.

When decarboxylation was carried out with quinoline and copper bronze, only one carboxyl group was removed to give a monocarboxylic acid of fluoranthene. This acid was different from fluoranthene-4-carboxylic acid which has been prepared by other means (18,32) so it was concluded that the acid was fluoranthene-3-carboxylic acid. Easton (32) found that the 4-carboxylic acid could be decarboxylated with copper bronze and quinoline. This work showed that the 3-carboxylic acid could not be decarboxylated under these conditions.

XXIII. Synthesis of 2-methylfluoranthene.

Maleic anhydride underwent condensation with 9-ethyl-9-hydroxyfluorene with greater difficulty. Only polymerisation occurred when acetic anhydride was used as a solvent but when boiling nitrobenzene was used, so giving a higher reaction temperature, the condensation proceeded smoothly. As in the case of 9-methyl-9-hydroxyfluorene, the reaction was accompanied by dehydrogenation. The dicarboxylic acid was too unstable to be isolated and no ester could be formed from this anhydride.

Decarboxylation was effected by heating with calcium hydroxide. 2-methylfluoranthene sublimed readily, showed a livid blue fluorescence in ultra violet light and formed an orange picrate.

By starting with fluorene compounds with other substituents in the 9- position, it seems likely that fluoranthene derivatives with substituents in the 2-position will be obtained. Difficulty may be experienced with some of these compounds, however, since 9-ethyl-9-hydroxyfluorene reacts less easily than 9-methyl-9-hydroxyfluorene and since it has been found that 9-benzalfluorene and 9-anisalfluorene did not react to form adducts (50).

XXIV Diels-Alder reaction on 2-ethyl-9-methyl-9-hydroxyfluorene.

In order to show the effect of nuclear substitution on this synthesis, 2-ethyl-9-methyl-9-hydroxyfluorene was prepared.

2-Acetylfluorene was reduced by a Clemmensen reduction to 2-ethylfluorene. On oxidation with molar quantity of sodium dichromate in glacial acetic acid, 2-ethylfluorenone was obtained along with a little 2-acetylfluorenone.

2-Ethylfluorenone underwent a Grignard reaction with methyl magnesium iodide. If the ether extract was evaporated to dryness at room temperature, the expected 2-ethyl-9-methyl-9-hydroxyfluorene was obtained. If, however, the ether was removed from a steam bath, dehydration occurred to give 2-ethyl-9-methylenefluorene which was quite stable and did not polymerise as readily as 9-methylenefluorene. Prolonged heating on the steam bath, however, caused the compound to polymerise to a resinous material. It was not expected that the addition of an ethyl group to the nucleus would influence the stability of 9-methylenefluorene to such an extent.

When 2-ethyl-9-methyl-9-hydroxyfluorene was refluxed

with maleic anhydride in acetic anhydride, polymerisation occurred and no adduct could be detected. With nitrobenzene as solvent, a resinous material was obtained. The failure of this compound to undergo a Diels-Alder reaction was rather surprising since an ethyl group would tend to activate the ring. There may, however, be some steric hindrance by the group to offset this activation. Even if the substituted ring was unable to take part in the reaction, it would be expected that the unsubstituted ring would condense as in the case of 9-methyl-9-hydroxyfluorene. It would seem, however, that polymerisation occurs much more readily than condensation so that a polymer is obtained as the sole product.

XXV Preparation of 3,4-benzfluoranthene-1':4'-quinone.

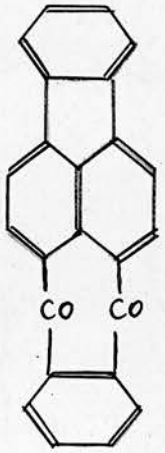
The Diels-Alder reaction with 9-methyl-9-hydroxyfluorene as the diene and with excess p-benzoquinone as dieneophil gave a quinone which must have the structure 3,4-benzfluoranthene-1':4'-quinone. The excess p-benzoquinone acted as dehydrogenating agent.

XXVI Preparation of 3,4:2',3'-naphthfluoranthene-1':4'-quinone.

In the same way, when excess 1:4-naphthoquinone was the dieneophil, the product could only be 3,4:2',3'-naphthfluoranthene-1':4'-quinone. Orange-red needles were obtained m.p. 249° - 251°C. This quinone gave a blue-violet vat with sodium hydrosulphite and a blue-green colour with concentrated sulphuric acid in the cold.

von Braun and Manz (19) claimed to have prepared this quinone by the cyclisation of 4-o-carboxybenzoyl-fluoranthene (see Introduction). Their compound, however, crystallised in yellow needles m.p. 328° - 331°C but gave a blue-violet vat with sodium hydrosulphite. It is clear that their compound is not identical with the quinone obtained in the present work and as there can be no doubt about the structure of the quinone from the Diels-Alder reaction the compound prepared by von Braun and Manz must have a different structure.

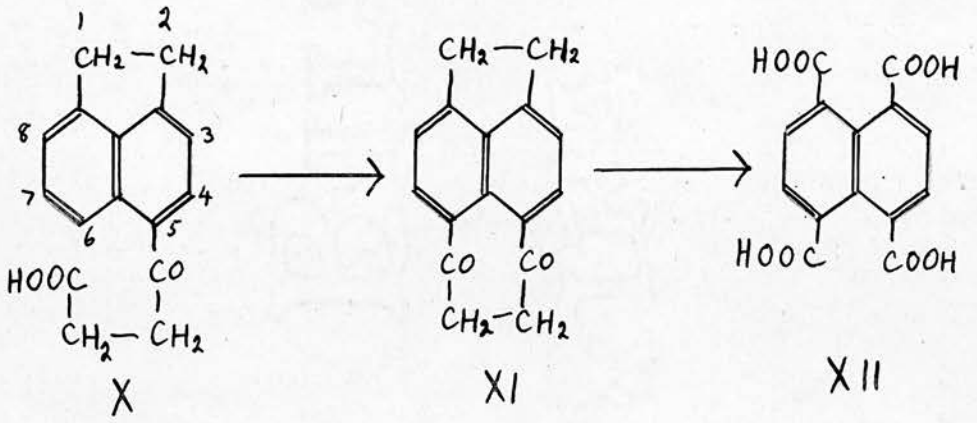
It is suggested that cyclisation occurred not at the 3- but at the 5- position to form 4:5-phthaloylfluoranthene IX.



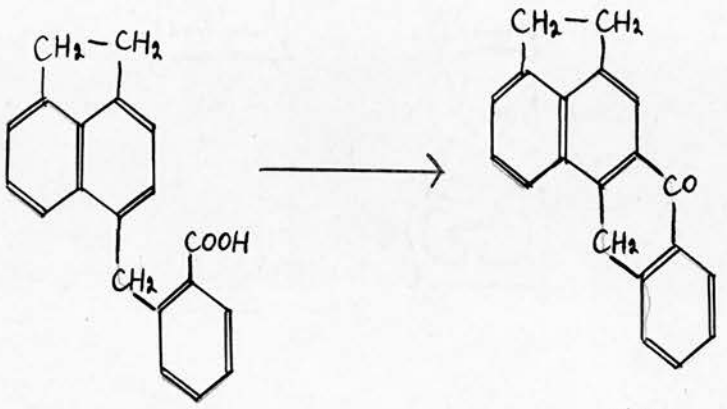
IX

It is known that the 'peri' positions of fluoranthene are very reactive and so the suggestion that a seven-membered ring is formed is feasible. von Braun and Manz did no work to prove the structure of their compound and it will be interesting to establish its structure.

Fieser and Peters (34) found that a Friedel-Crafts reaction on acenaphthene with succinic anhydride formed β-(5-acenaphthoyl)propionic acid X, which on fusion with molten aluminium chloride at 150°C led to the closure of a seven-membered ring to give peri-succinoylacenaphthene XI, a yellow alkali-insoluble compound. The structure of this compound was shown through oxidation to naphthalene-1:4:5:8-tetracarboxylic acid XII.

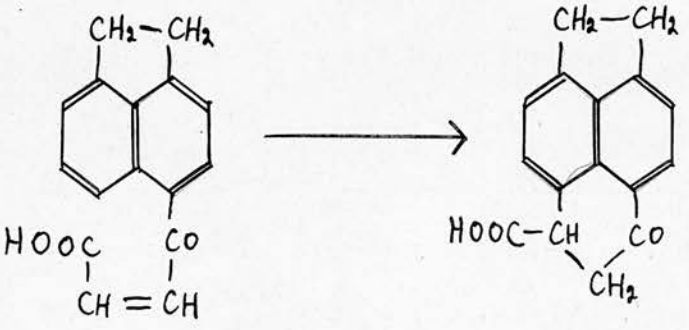


The formation of a seven-membered ring, especially where the closure to a six-membered ring is also possible, is very difficult. In this case, the closure of a six-membered ring would involve substitution at a position 'ortho' to an unsaturated group and Fieser and Peters thought that this factor probably impeded the reaction. The closure of a seven-membered ring through a 'peri' condensation, on the other hand, would be facilitated by the presence of the dimethylene bridge. This idea on the effect at a position 'ortho' to an unsaturated group is supported by the work of Cook (20), who found that 5-acenaphthylphenylmethane-2'-carboxylic acid XIII was cyclodehydrated to acenaphthanthracene XIV, thus showing that substitution occurred more easily at position 4- than at 6- when no such group was present.



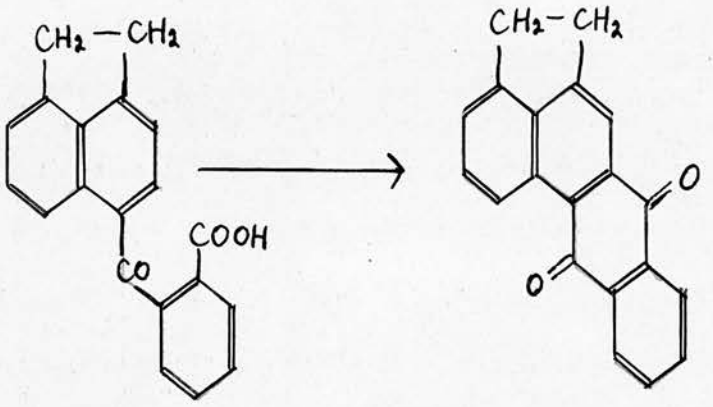
XIII XIV

Fieser and Peters (34) also prepared β-(5-acenaphthoyl)acrylic acid XV which they condensed with aluminium chloride to give a product which had the probable structure XVI.



XV XVI

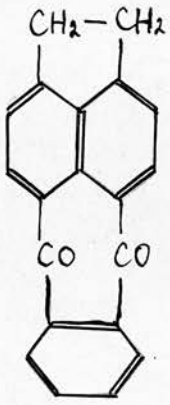
5-o-carboxybenzoylacenaphthene XVII has been prepared by Graebe and Perutz (36). They found that this acid underwent cyclisation to give a greenish-yellow compound (m.p. 215° - 220° C) which they concluded was the acenaphthanthraquinone XVIII through analogy to the formation of 1:2-benzanthraquinone XX from α-o-carboxybenzoylnaphthalene.



XVII XVIII

No attempt was made to prove this structure.

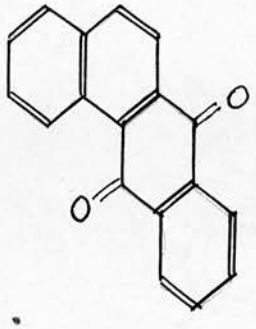
In view of the above, it is suggested that this compound may have undergone 'peri' condensation to give the compound XIX.



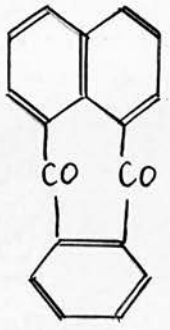
XIX

Work on this subject, at present being carried out in the department, has confirmed this suggestion.

α-o-carboxybenzoylnaphthalene and its derivatives have been shown by numerous workers to cyclise to 1:2-benzanthraquinones. Rieche, Sauthoff and Müller (46), however, found that naphthalene condensed with phthalic anhydride under certain conditions to give a mixture of 1:2-benzanthraquinone XX and 1:8-phthaloylnaphthalene XXI. The structure of the latter compound was proved conclusively.



XX



XXI

The fact that naphthalene, although its 'peri' positions are not so reactive as in acenaphthene and fluoranthene, gives a peri-condensation product, lends further support to the above suggestion on the phthaloylation of acenaphthene and fluoranthene.

Possible extensions and limitations of the Diels-Alder Synthesis.

The preceeding synthesis of fluoranthene has been shown to be capable of extension.

(a) By starting with other 9-substituted 9-hydroxyfluorenes, it is possible to introduce substituents in the 2- position of fluoranthene. As has already been pointed out, there is a reduction in the reactivity so that there will be a limit to the extension in this direction.

(b) Dieneophils, other than maleic anhydride, have been found to be reactive in this synthesis. By condensing with various dieneophils, it may be possible to synthesise other fluoranthene derivatives. As there are two competing reactions, it will be necessary to employ quite reactive dieneophils, thus limiting the

choice of reactant.

(c) The one case of nuclear substituted fluorene tried, has been found to undergo polymerisation only. Nevertheless, it appears likely that some nuclear substituted fluorene compounds will yield the desired condensation products. If this is accomplished, it will be possible to synthesise the mono and disubstituted fluoranthenes already prepared. In particular, it will be possible to determine unambiguously the constitution of disubstituted products, By starting with 2:7-derivatives of fluorene, which are comparatively easy to prepare, 4:11-derivatives of fluoranthene will be synthesised. As disubstitution is believed to occur in the 4:11- positions (see Introduction), the positions of disubstitution will then be proved.

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